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THE ABSORPTION SPECTRA OF SOLUTIONS AS AFFECTED BY TEMPERATURE AND BY DILUTION. A QUANTITATIVE STUDY OF ABSORPTION SPECTRA BY MEANS OF THE RADIO-MICROMETER

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INTRODUCTION

An investigation on the effect of temperature on the absorption spectra of certain solutions has already been carried out by Jones and Strong.¹ The apparatus used was devised by Professor John A. Anderson,² who worked somewhat earlier with Jones³ on the absorption spectra of solutions. The solutions were heated in an open vessel, and the temperature could, of course, not be raised much above one hundred degrees. It was found that even over this range in temperature the effect of rising temperature was to cause the general

¹ Carnegie Institution of Washington, Publication 130. *THIS JOURNAL*, 43, 37, 97 (1910); 45, 1, 113 (1911).

² Carnegie Institution of Washington, Publication 130.

³ Carnegie Institution of Washington, Publication 110, p. 20. *THIS JOURNAL*, 41, 276 (1909).

absorption of any salt in water to increase, and also to cause the bands to broaden and become more intense.

The results were entirely unambiguous as far as they went, but they were limited by the boiling points of the solutions in question. Indeed, it was not possible to work quite up to the boiling point of the solution, since the change in the concentration of the solution resulting from boiling would have been too great, and there would have been too much gas formed on the quartz windows through which the light was to pass.

We wanted to study the effect of rise in temperature on the absorption spectra of solutions to as high temperatures as it was possible to go. For this purpose closed forms of apparatus devised by Anderson¹ and by Strong² were employed by Jones and Strong³ for nonaqueous solutions. The apparatus consisted of a gold-plated steel tube, whose ends were closed with glass windows. This worked very well with nonaqueous solvents up to temperatures of approximately 200° C. Usually before this temperature was reached a precipitate formed in the tube, which prevented work at higher temperatures.

Some interesting results were obtained at the higher temperatures with this apparatus. The general effect of rise in temperature is to deepen the color of the solution of an inorganic salt. This is usually due to a widening of the absorption bands. For details in reference to the effect of temperature on the absorption of light by nonaqueous solutions reference must be had to the Carnegie monograph,⁴ where the results in question are published in full.

The apparatus used by Jones and Strong for nonaqueous solutions did not work satisfactorily for solutions in water as the solvent. The water vapor, under the high pressure produced within the apparatus, worked its way through the layer of gold laid down on a layer of copper electrolytically,

¹ Carnegie Institution of Washington, Publication 100, p. 28. *THIS JOURNAL*, 47, 30 (1912).

² Carnegie Institution of Washington, Publication 100, p. 29. *THIS JOURNAL*, 47, 30 (1912).

³ Carnegie Institution of Washington, Publication 100. *THIS JOURNAL*, 47, 27, 126 (1912).

⁴ Carnegie Institution of Washington, Publication 100.

rusted the steel and caused the separation of the gold from the steel walls.

To avoid this, the apparatus, which was designed by Dr. Strong,¹ was made of brass and will be described in some detail later in the paper. It was plated electrolytically with gold and this adhered firmly to the brass even when the aqueous solution contained in the apparatus was heated to 200° C. We could work as satisfactorily with this apparatus with aqueous solutions as with the former apparatus with non-aqueous solutions. The work described in this paper on the absorption spectra of aqueous solutions at high temperatures was all carried out in the gold-plated, brass apparatus. The results obtained and the bearing of these results on the nature of solution will be discussed in the proper place in this paper. Suffice it to say here that the effect of temperature up to 200° on the absorption spectra of aqueous and nonaqueous solutions has now been studied pretty extensively on a large number of salts and a fairly large number of solvents.

The effect of dilution on the absorption spectra of solutions was taken up with the following idea in mind. It was long a question as to what is the nature of the absorber of light, say in aqueous solutions. It was at one time supposed that chemical molecules are the absorbers, since these were regarded as the ultimate units in solution. It was supposed that the molecules were thrown into resonance by certain wave lengths of light, and these were, consequently, stopped, while the remaining wave lengths passed through the solution and gave to it its characteristic color.

When the theory of electrolytic dissociation was proposed in 1886, the view as to the nature of solutions of electrolytes underwent a serious change. When electrolytes were dissolved in water, or in any other dissociating solvent, they dissociated into charged parts or ions, and these were the ultimate units in solution. If the solution was fairly concentrated we had both ions and undissociated molecules in the solution, and the question in such cases was, which is the absorber?

¹ Carnegie Institution of Washington, Publication 180. *THIS JOURNAL*, 47, 30 (1912).

It was further recognized that a dilute solution of a salt often has very different color from a concentrated solution; and, moreover, solutions of nonelectrolytes are often colored, i. e., have the power to absorb certain wave lengths of light and to allow others to pass on through. It was supposed then that molecules have the power to absorb light, and ions also have absorbing power. When a concentrated and a dilute solution of an electrolyte had the same absorption spectrum—the same color—it was supposed that the chemical molecule and the ions resulting from it had the same absorption. When the dilute solution had a different color from the concentrated solution, it was supposed that the ions were the chief absorbers of light. And since it frequently happens that a dilute solution of an electrolyte has a very different color from a more concentrated solution, it was supposed that in dilute solutions of electrolytes the ions are the chief absorbers of light; since in very dilute solutions of electrolytes there are mainly ions and practically no molecules present, it is obvious that in such solutions it is not the molecules which are absorbing light. It must be the ions, since these are the only units present, or something contained within the ions. This was the view of absorption of light introduced by the theory of electrolytic dissociation.

We have now gone much farther than this. We now know that the ions are not the ultimate units in a solution of an electrolyte. The simplest ion is very complex. It is made up of a large number of electrons, which are unit negative charges of electricity. There is every reason to-day to believe that the electrons are the real absorbers of light, are the units which are thrown into resonance by the various wave lengths of light. Granting this, there is still a difference between an ion and the atom or atoms from which it was formed. An ion contains one or more free electrons within it, i. e., one or more negative charges than would correspond to the positive electricity within the atom. It would be interesting to know whether the free electron or electrons upon the ion have anything to do with its power to absorb light. This can be tested by studying the absorbing power of molecules and then the

absorption of light by the ions which are formed when these molecules dissociate. It was with this idea in mind that the second chapter of the work described in this paper was undertaken.

A concentrated solution of a salt contains many molecules, and if the solution is sufficiently concentrated there are chiefly molecules and only a few ions present. As the dilution is increased the dissociation increases, the number of molecules becomes less and less and the number of ions greater and greater. The problem then is to photograph the absorption spectrum of a very concentrated solution of a salt, the layer being, say, 0.5 cm. deep. Then take the spectrum of a more dilute solution of the same salt; if the dilution is increased one hundred times the depth of layer used would be fifty cm. Under these conditions there would be the same number of parts of dissolved substance in the path of the beam of light; in the second case, there would be more ions and less molecules than in the first. By comparing the two spectra we could see whether there is any difference between the absorbing power of ions and molecules, i. e., whether the free electrons upon the ions have anything to do with their power to absorb light. We then took another step, increasing the dilution of the second solution five times and also increasing the depth of the layer of the solution through which the light passed five times, i. e., making the depth 250 cm. This second diluting still further reduced the number of molecules present and increased the number of ions. By comparing the three spectrograms we ought to be able to say whether molecules and ions have the same or different resonance with respect to light waves, and, if it is different, to point out in what the difference consists. This would then enable us to determine whether the free electrons upon the ions played any part in the absorption of light.

We shall see that ions have somewhat different absorbing powers from molecules, and in what this difference consists will appear later from the text and from the plates.

The work done on the absorption spectra of solutions by

Jones and Uhler,¹ Jones and Anderson,² and Jones and Strong,³ which extended over five years, and in which some 6000 solutions were studied, all involved the photographing of the various spectra. In this way the positions of the various absorption lines and bands were determined.

A question even more fundamental than the positions of the lines and bands is their intensities, and the relative intensities of different parts of the same band. The photographic method gave only a means of dealing qualitatively with this problem. Some general idea could be gained of the relative intensities of the various lines and bands on the photographic plate, but these changed with the time of exposure, the intensity of the light used and with other conditions, so that we were able to learn very little about the intensities of the various lines and bands by means of the photographic method.

Further, the photographic plate is sensitive only between the wave lengths 2000 Å.U. and 7600 Å.U., which is a comparatively small part of the spectrum. It is especially important to work also into the region of the infrared.

A method was used which dealt quantitatively with the intensities of the various lines and bands. This same method, instead of being limited by the above-named wave lengths, could be used down into the infrared to wave lengths as great as 20000 Å.U. to 30000 Å.U. Indeed, the method can be used for even greater wave lengths, if solvents can be found that are transparent to the longer waves. This method involves the use of the radiomicrometer.

The description of the instrument which we built, the method of work, and the results thus far obtained, will be given in the third section of this paper.

THE ABSORPTION SPECTRA OF AQUEOUS SOLUTIONS AS AFFECTED BY TEMPERATURE

Jones and Strong⁴ studied the effect of temperature on the

¹ Carnegie Institution of Washington, Publication 60. *THIS JOURNAL*, **37**, 126, 207 (1907).

² Carnegie Institution of Washington, Publication 110. *THIS JOURNAL*, *Loc. cit.*

³ Carnegie Institution of Washington, Publications 130 and 180. *THIS JOURNAL*, *Loc. cit.*

⁴ *THIS JOURNAL*, **47**, 27, 126 (1912).

absorption spectra of various nonaqueous solutions up to nearly 200° . The solutions were usually heated until a precipitate formed, which cut off the light and prevented work at still higher temperatures. Some work was also done by Jones and Strong on the effect of temperature on the absorption spectra of aqueous solutions. This was, however, not large in amount and did not extend to very high temperatures.

The reason that the work was not pushed to higher temperatures, with aqueous solutions, was that the form of apparatus then in use did not admit of it. This consisted of a steel tube,¹ lined on the inside with copper and plated with gold on all of the inner surfaces. This worked very satisfactorily with nonaqueous solutions, the gold plate adhering firmly to the copper, which, in turn, remained adherent to the steel.

When an aqueous solution was heated in the apparatus from 100° to 200° the result was unsatisfactory. The water, under the high pressure, forced its way through the copper and the gold and rusted the iron, as has already been stated. The result was that the copper, with the gold, separated from the steel, and the solutions, after heating for a time, gave the iron reaction. This apparatus had the further disadvantage that when a precipitate formed with rising temperature it was necessary to open the entire apparatus and remove the glass ends in order to clean them.

To overcome these difficulties the following form of apparatus (Fig. A) was constructed and used to study the effect of rising temperature on the absorption spectra of aqueous solutions.

The quartz ends are fastened into the ends E' . The plunger P has guide grooves instead of guide pins. A part of the plunger is provided with screw threads for removing it. The entire cap is removed from tube T by unscrewing E' , during which the quartz end is untouched. When the ends are removed the quartz window can be easily cleaned. Gold washers were inserted between T and E' and between E' and U .

¹ THIS JOURNAL, 47, 30 (1912).

The general arrangement of the apparatus is also shown in Fig. A. The cell is kept in a horizontal position so that any bubbles that may form will rise in the side tube. The spectro-scope, containing the grating *G*, photographic plate holder *C*, and slit *S*, being kept vertically, a 45° quartz prism was used to change the horizontal beam of light into a vertical beam, the beam being totally reflected by the hypotenuse surface of *O*. The source of light *NG* (Nernst glower) or *SG* (spark gap) was focused by the concave speculum mirror *M* on the slit *S*. A similar arrangement was used for the fused silica cell. *DTS* is a double throw switch, by means of which either the Nernst glower or the spark gap may be thrown in circuit. *B* is a ballast. *R* is a variable resistance, by means of which the current in the Nernst glower, as shown by the ammeter *A*, may be kept constant. *OC* is an oil condenser. *IC* is an X-ray induction coil and *R₁* is a resistance in the primary circuit of this coil. In a recent paper Merton¹ states that he has studied the effect of pressure on the absorption spectra of solutions. This was studied here and the results published in *THIS JOURNAL*,² the quotation of a paragraph from our earlier paper will show what was found:

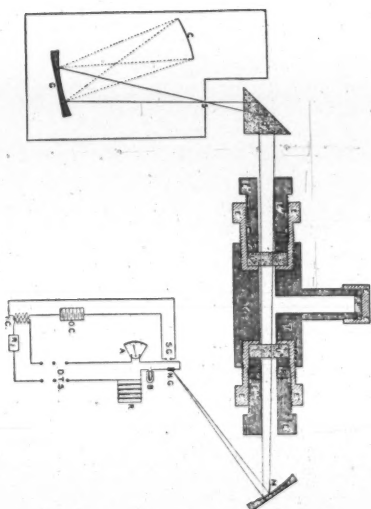
"Some preliminary tests were made with the cells at high pressures. The Cailletet pump belonging to the University was used for this purpose, the cell being made so as to fit into this pump. It was not at all difficult to obtain pressures of 200 atmospheres with water and alcohol solutions. Spectrograms were made of the absorption spectra of neodymium solutions under pressures as high as 275 atmospheres. *No effect of pressure was detected.* The work at high pressures is easier than at high temperatures, on account of the fact that there is an expansion of the cell due to heating.

It should be stated that in all of the work on absorption spectra which has been carried out in this laboratory for the past seven years, a grating spectroscope has been used. The arrangement of the heated cell, the grating, photographic plate, etc., will now be discussed.

¹ P. Roy. Soc., (A) **87**, 146.

² Vol. **47**, page 32, January, 1912.

Fig. A.



Discussion of Some of the Results Obtained

The description of a few of the spectrograms obtained is given in the following pages. The plates as a whole will probably be published in the near future as a monograph by the Carnegie Institution of Washington.

The Making of a Spectrogram

The apparatus used throughout the entire study of the effect of high temperature has already been discussed. Two cells were used, one ten cm. and the other one cm. in length, both having the same general design and differing only in length.

The cell, placed in a suitable bath for keeping the temperature constant, was arranged as indicated in the diagram and the source of light so located that the rays, reflected from a concave mirror, passed longitudinally through the cell and formed an image of the Nernst glower on the slit of the camera. The position of the prism is so adjusted as to fill the grating uniformly with light. Holding the eye directly above the grating, in a position later to be occupied by the photographic plate, we could easily tell when the proper light was falling upon the grating. When the cell was in its proper adjustment the lights were extinguished and the photographic plate inserted. With the plate in position, the light was turned on and an exposure made at room temperature. The position of the plate was then moved a given distance, and the temperature of the cell raised very slowly, this process being repeated at intervals of about 20° or 25° .

It is clear that, with such pressures as are developed by heating water to 200° , it is very difficult to obtain a tight joint between glass and metal. This difficulty, however, has been partially overcome by the special form of apparatus designed by Dr. Strong and described elsewhere in this paper. We were not able to secure a closing that would hold above 200° , but once a good closing was secured it was not necessary to remove the ends for several operations.

Great care had to be taken in heating the cell, on account of the difference in expansion of the glass ends and the metal

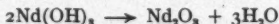
in contact with them. When the temperature was raised more than 40° an hour the glass ends usually broke. At such high temperatures as we were employing the glass was rapidly attacked by the water and afterwards, when we were using the clear uivole glass, a single heating rendered the glass ends almost opaque, especially if they were allowed to stand any length of time.

It was found that in many cases precipitates would appear in the cell at a temperature slightly above 100° . This precipitate, however, formed rapidly, once it began, and almost as quickly disappeared. By properly regulating the intervals at which exposures were made, the effect of the precipitate could be avoided; hence this effect does not appear on any of the strips photographed.

It is probable that at first slight hydrolysis took place, as



The presence, then, of a slight excess of hydrochloric acid would hinder the reaction in the direction indicated above by the arrow. Since most hydroxides lose water at temperatures above 100° , it is possible that the following reaction would take place:

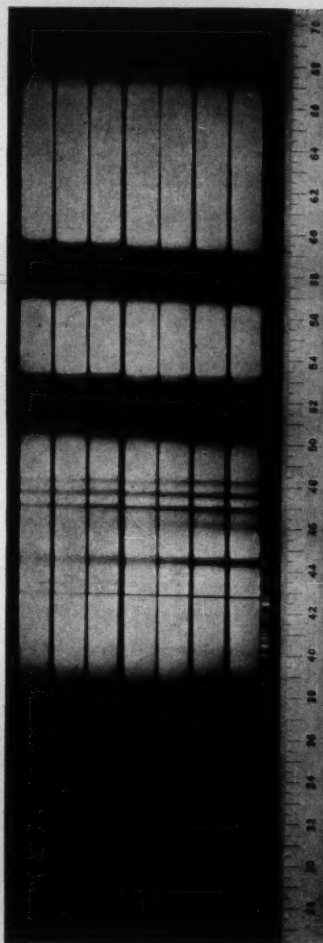


The neodymium oxide, being heavy and very slightly soluble in water, settles to the bottom of the cell, and the solution clears up. In this way, it is evident, our solution becomes slightly more dilute as the temperature is raised, but this would lessen the number of absorbers in the path of the beam of light, and thereby produce a narrowing of the bands; it could only decrease the effect indicated in the films. This antagonistic influence could certainly not cause a widening of the absorption bands with rise in temperature.

Neodymium Chloride in Water (see Plate I)

The solution whose spectrum is given in Section A was saturated, the depth of absorbing layer being 1 cm. The temperatures, beginning with the strip nearest the numbered

A



B

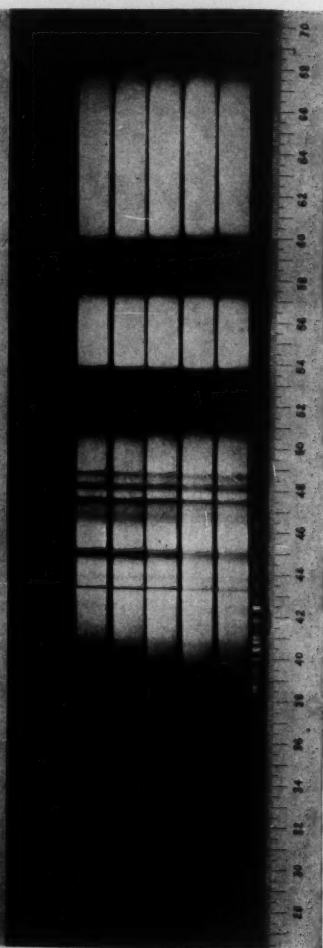


Plate I

scale, were 20° , 45° , 70° , 95° , 115° , 140° and 165° , respectively.

Absorption bands which are unchanged by the range of temperature from 20° to 200° appear at $\lambda 3800$, $\lambda 4025$, $\lambda 4200$, $\lambda 4325$, $\lambda 4440$, $\lambda 4600$, $\lambda 4690$, $\lambda 4750$ and $\lambda 4820$.

The double band from $\lambda 5050$ to $\lambda 5270$ is only slightly affected, if at all.

The two most interesting absorption bands are those whose centers are near $\lambda 4275$ and $\lambda 5800$. The former of these in Strip 1 is very sharp and intense, though only a few Å.U. wide. Both edges were well defined. As the temperature is raised the violet edge remains very sharp, while a rapid shading off of the red edge takes place. At a glance the band appears to be less intense in the higher temperature strips, but on close examination it is seen to be more diffuse, the red edge diffusing over a range of about 20 Å.U. at the highest temperature. This is exactly in accord with what Jones and Anderson¹ had found. They showed that when the number of molecules in the path of light was kept constant, this band remained practically constant, while it has been shown by Jones and Anderson and by ourselves that this band changes with dilution, being more intense in the most concentrated solution.

The $\lambda 5800$ band is affected most by temperature as well as by dilution. In Strip 1 this band is about 200 Å.U. wide, and increases regularly in width as the temperature is raised, until at the highest temperature the width is over 250 Å.U., or there is a total widening of 50 Å.U. The violet edge remains perfectly sharp, while the shading is towards the red end of the spectrum.

It occurred to us that whatever effect might be produced by a rise in temperature, if it was a true temperature effect, the reverse should happen when the solution was allowed to cool.

With this in view *B* was made. The concentration of the solution and the depth of layer photographed in Section *B* were exactly the same as in *A*. In fact, the identical solution

¹ Carnegie Institution of Washington, Publication 110.

was used. As soon as the film *A* had been exposed with rising temperature, it was removed from the camera and developed. Without even allowing the cell to cool, another film was placed in the camera and Section *B* made with falling temperature. In *B* the temperatures were 165° , 140° , 115° , 95° and 70° , the highest temperature being nearest the numbered scale.

A study of the original film shows changes only in bands λ_{4275} and λ_{5800} ; and this change is exactly the reverse of that shown by these same bands in *A*. The λ_{4275} band appears in Strip 1 with a sharp violet edge and shading off toward the red over a range of 15 or 20 Å.U. As we pass to the succeeding strips in the direction of falling temperature the red edge becomes sharper and sharper until, in Strip 3, which represents the lowest temperature, the band assumes its normal sharp edge on the red side and covers less than ten Å.U. The λ_{5800} band narrows uniformly from the red end, as the temperature falls, the total narrowing being about 40 Å.U.

Neodymium Bromide in Water (see Plate II)

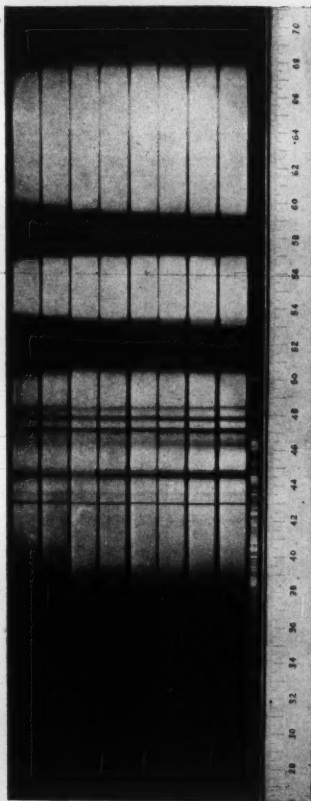
The concentration of the solution used in making the negative for *A* was 1.66 normal; the depth of cell, 1 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20° , 45° , 70° , 95° , 120° , 140° , 175° and 190° , respectively.

This plate seems to have had just the proper length of exposure for the given concentration, and every known neodymium absorption band appears on the negative in excellent condition. With the bromide, as with the chloride discussed in Plate I, only λ_{4275} and λ_{5800} show changes with rise in temperature. The λ_{4275} band, which has both violet and red edges sharp in Strip 1, feathers out toward the red end of the spectrum as the temperature is raised.

The λ_{5800} band widens toward the red as much as 60 Å.U.

The concentration of solution used in making *B* was 0.166 normal, one-tenth that of *A*; the depth of absorbing layer was 10 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20° , 45° , 70° , 95° , 115° , 135° , 155°

A



B

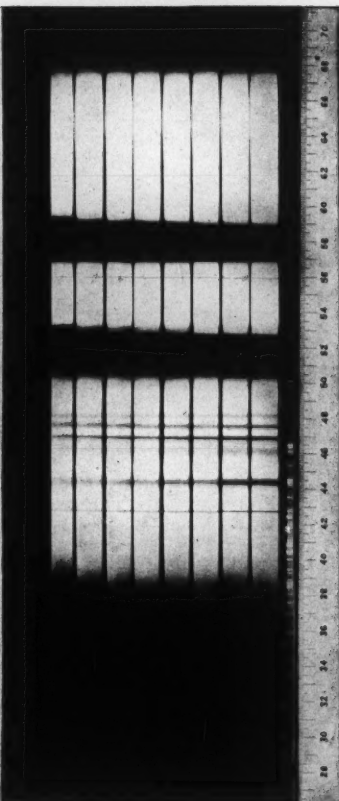


Plate II

A

B

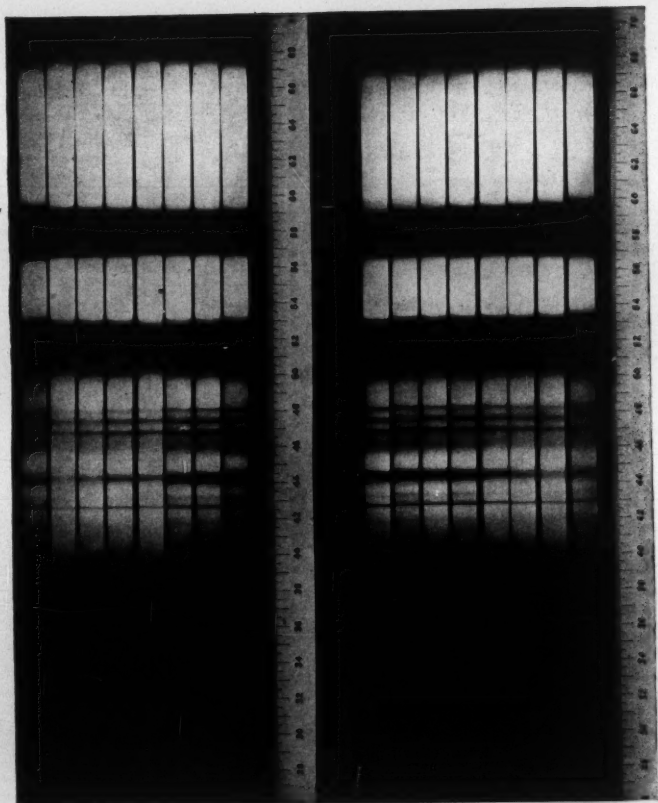


Plate III

and 190° , respectively. This is probably the best negative produced in this part of the work, and the bands $\lambda 4275$ and $\lambda 5800$ show well the characteristic changes spoken of above. The widening of band $\lambda 5800$, though well marked, is not so great as in *A*, the total change being about $40 \text{ \AA.U.}$, as compared with $60 \text{ \AA.U.}$ in the former.

If such a band be due to molecules this is what we should expect, since, *B* being a more dilute solution, the total number of molecules is less than in *A*. Hence, any change associated with molecules would be more clearly apparent in *A*.

This is in accord with changes produced in this same band by dilution.

Neodymium Nitrate in Water (see Plate III)

The concentration of the solution used in making the negatives of *A* was one-tenth of saturation, the depth of absorbing layer 10 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20° , 45° , 70° , 95° , 115° , 140° , 165° and 190° .

Aside from the slight tendency for all the absorption bands to become a little more diffuse, though not more intense, at the higher temperatures, there is no marked change in any band except $\lambda 4275$ and $\lambda 5800$. The former of these, as we go toward the higher temperatures, remains perfectly sharp and constant on its violet edge, while there is a regular shading towards the red end of the spectrum. Again, the greatest change takes place in band $\lambda 5800$, the violet end remaining fixed and the red edge widening between the first and last strips to the extent of about $50 \text{ \AA.U.}$ All the exposures of this plate were made as the temperature of the cell was raised.

The identical solution used above was photographed in *B*—the cell, intensity of light source, and all of the apparatus, remaining unchanged, the only difference being that the exposures of *B* were made at regular intervals as the temperature of the cell was *lowered*. The temperatures of the successive strips in *B* were, beginning with the strip nearest the numbered scale, 190° , 165° , 140° , 115° , 95° , 70° , 45° , 20° .

The original films show *A* and *B* to be exactly the reverse

of each other. Just those changes produced in *A* by a rise in temperature are reversed by the corresponding fall of temperature in *B*. Of course, this is only qualitative, since we can establish no definite quantitative relations from the photographic plates. In order to do this, energy measurements must be made, not only on each band, but on different parts of the same band. Such work is now in progress. This, of course, would be very difficult to do with a narrow band like λ_{4275} , but should be comparatively simple with band λ_{5800} .

Band λ_{4275} , which, in Strip 1, appears broad and hazy on its red edge, gradually acquires the characteristic sharp intense edges as the temperature falls, until, in Strip 8, it is only about 8 Å.U. wide. The total change in band λ_{5800} is a narrowing of about 60 Å.U. There is no sudden or decided change between any two successive strips, but, on the contrary, so far as the photographic plate is able to show, the change is a gradual one.

Neodymium Acetate in Water (see Plate IV)

In Plate IV we have photographed the change in the absorption bands of neodymium acetate, produced by rise in temperature, Section *A*, and by the corresponding lowering of temperature, Section *B*. The concentration of the solution used for both negatives was one-tenth of saturation; the depth of absorbing layer, 10 cm.

The temperatures of the strips in *A*, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 120°, 140°, 160°, 190°. This negative shows changes in bands λ_{4275} and λ_{5800} ; the former, as in the other plates on the study of the effect of temperature, shows a marked shading toward the red, while the remainder of this band virtually remains fixed. The λ_{5800} band widens rapidly towards the red, as the temperature is raised, the total amount being about 80 Å.U. All the absorption bands with the acetate are more intense and broader than for the same concentration of any of the other salts of neodymium studied. The acetate is not nearly so soluble as the other salts, nor is the dis-

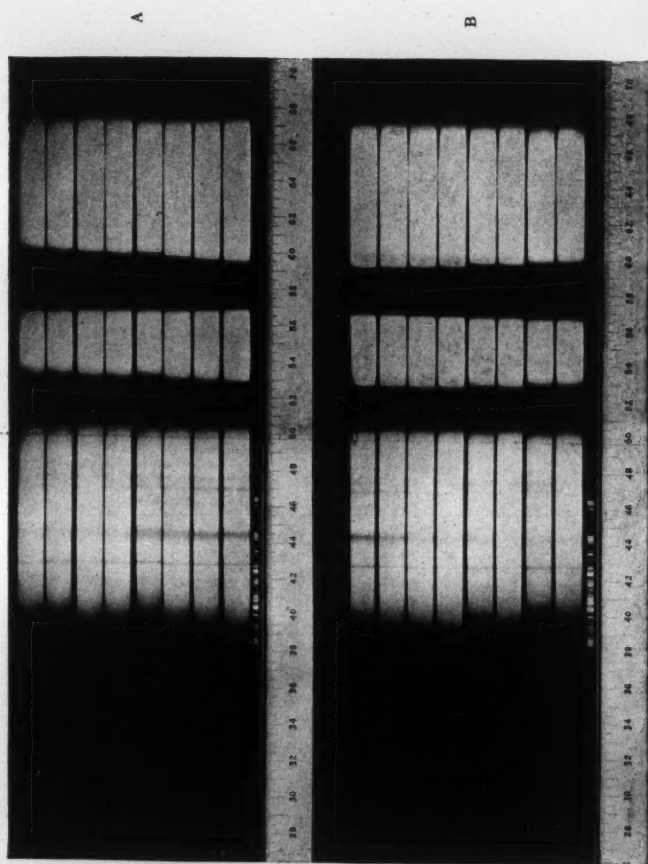


Plate IV

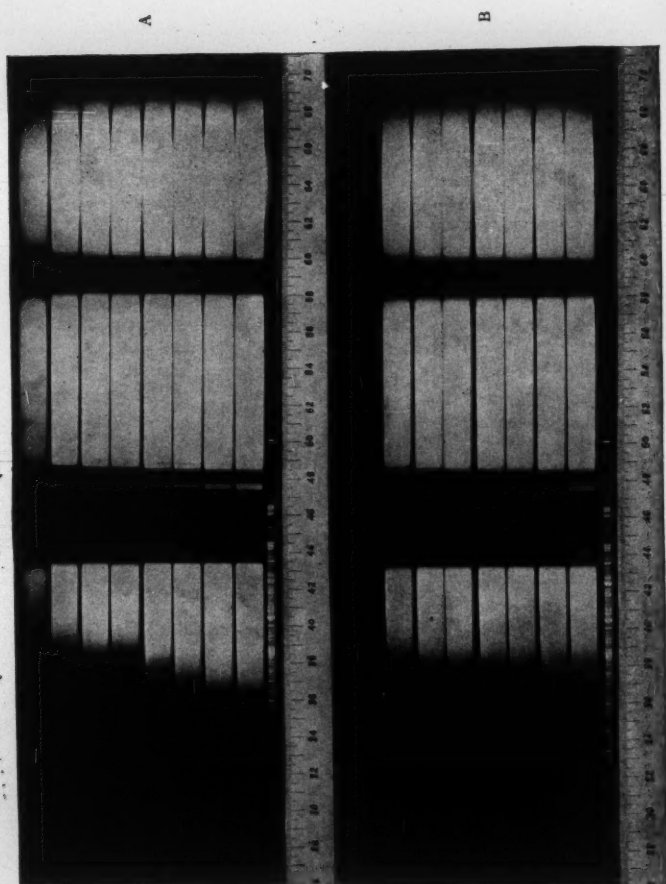


Plate V

sociation so great, yet we find in *A*, which is the spectrogram of a one-tenth saturated solution of neodymium acetate, greater changes than for the saturated solution of the chloride. This is in accord with the results obtained from the effect of dilution: this, it will be seen, was greatest with the acetate. This tends to strengthen the view that the bands λ_{4275} and λ_{5800} are in some way associated with the molecules.

In *B* of this plate there is given the spectrogram of the same solution as the temperature was lowered. The temperatures, beginning with the strip nearest the spark spectrum, were 190° , 165° , 145° , 125° , 100° , 75° , 50° , 25° ; the cell and arrangement of apparatus were the same as in *A*. The negative shows changes the reverse of those discussed in Section *A*. The λ_{4275} band gradually assumes the sharply defined edges as the temperature falls, and Strip 8 of *B* corresponds exactly to Strip 1 of *A*. In a word, there has been no permanent change produced by heating the solution. This change in the width of the absorption bands could not have been produced by any substance dissolved from any parts of the apparatus, as there is no reason to suppose that this should disappear as the solution was cooled. It seems, then, that the broadening is solely a temperature phenomenon.

Praseodymium Nitrate in Water (see Plate V)

The concentration of the solution used in making *A* was 2.6 normal; the depth of cell, 1 cm. The temperatures, beginning with the strip nearest the numbered scale, were 12° , 32° , 52° , 72° , 92° , 112° , 125° and 145° , respectively.

In the ultraviolet the absorption extends to about λ_{3500} in Strip 1, but rapidly increases as the temperature is raised, until in Strip 8 there is complete absorption as far as λ_{3800} .

There is a very intense double absorption band from λ_{4350} to λ_{4725} with faint transmission near λ_{540} . This transmission rapidly decreases as the temperature is raised, and entirely disappears at a temperature slightly above 100° . The λ_{4650} band widens toward the red end about 25 Å.U. Band λ_{4825} shows a total widening of about 30 Å.U. over the range of temperature studied. The orange band near λ_{5900} shows a uniform total widening of about 25 Å.U.

From this plate it is seen that none of the praseodymium bands show very marked change with rise in temperature. It may be stated that, at this concentration, all of them become slightly wider at the higher temperatures.

In Section *B* of this plate is given the spectrogram of a 0.26 normal solution of the same salt, the depth of the absorbing layer being 10 cm. The temperatures, beginning with the strip nearest the numbered scale, were 20°, 45°, 70°, 95°, 115°, 135° and 165°, respectively.

There appear on this plate bands which have their centers near $\lambda 4425$, $\lambda 4650$, $\lambda 4825$ and $\lambda 5900$; the ultraviolet absorption bands near $\lambda 3500$. None of these bands show any appreciable change over the range from 20° to 165°.

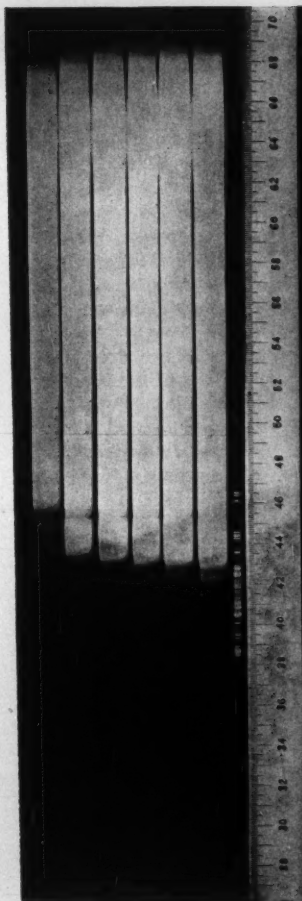
The plate which was used to study the effect of dilution upon this same salt reveals the fact that only in the most concentrated solutions were the bands affected at all, while in the dilute solutions all the bands remained unchanged. It is seen from Plate V, discussed above, that temperature also has a slight effect only in the concentrated solutions, while in the dilute solutions the bands remain unchanged. In a word, rise in temperature and decrease in dilution produce the same effect upon solutions of praseodymium nitrate.

Uranyl Nitrate in Water (see Plate VI)

The concentration of the solution used in making *A* was 0.2 normal, the depth of layer being 1 cm. The temperatures, beginning with the strip nearest the spark spectrum, were 20°, 40°, 60°, 80°, 100° and 120°, respectively. In every strip the exposure to the entire spectrum was made for thirty seconds, a screen cutting off all wave lengths beyond $\lambda 4500$ was inserted and the ultraviolet end exposed an additional eight minutes.

Since all the uranyl bands occur in the violet and ultraviolet end of the spectrum where the general absorption is greatest, due to precipitates formed by heating the solutions, etc., it was found very difficult to obtain satisfactory results. So far as this plate shows there is no decided change in any particular band. The entire series seems to widen as the tem-

A



B

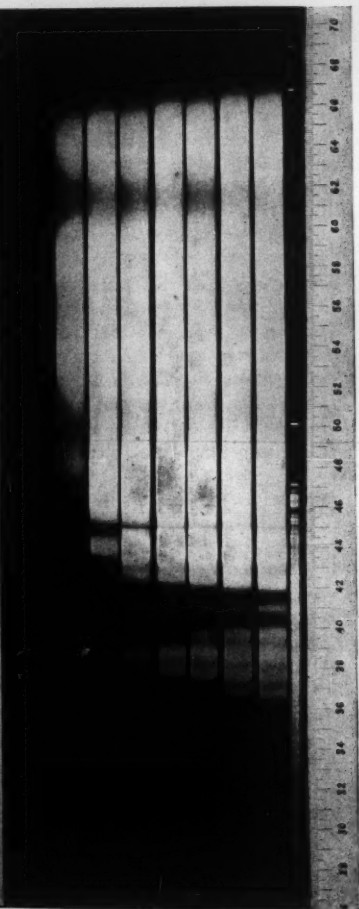


Plate VI

perature is raised, and at the same time the center of the band is slightly shifted toward the red end of the spectrum. The general absorption, ending near $\lambda 3500$, in Strip 1, advances rapidly toward the red as the temperature is raised. The broad diffuse edges of all the bands shade uniformly into each other, until at the highest temperature they appear as one broad hazy absorption band, extending from $\lambda 3800$ to $\lambda 4300$. At least a part of this is due to general absorption.

In Section B is given the absorption of a 0.02 normal solution of uranyl nitrate, the depth of absorbing layer being 10 cm. The red end of the spectrum, beyond $\lambda 4500$, was exposed eight seconds, while the ultraviolet below $\lambda 4500$ had an exposure of three and one-half minutes to the same source of light. The temperatures, beginning with the strip nearest the numbered scale, were 20° , 45° , 70° , 95° , 115° , 140° and 165° , respectively. There are eleven bands occurring between $\lambda 3500$ and $\lambda 4600$. As the temperature is raised all the bands become more diffuse and broader. The band whose center is near $\lambda 4180$ seems to be most affected. The red edge of the band shades toward the red end of the spectrum as much as 25 Å.U. The effect produced on this band by elevated temperatures is more marked than in any of the other bands. There is very broad and hazy absorption around $\lambda 5100$, $\lambda 5600$ and $\lambda 6200$. This increases with rise in temperature.

It has been found very difficult to give an exact description of what takes place in any uranyl band as the temperature is raised, since the edges of the bands are so hazy and the general absorption so marked in the region of the spectrum at which these bands occur. Only the general statement can be made that all uranyl bands become more diffuse with rise in temperature, and in one case, i. e., the band $\lambda 4165$, there is a decided shading on the red edge.

Uranyl Sulphate in Water (see Plate VII)

The concentration of the solution used in making A was 0.166 normal and the depth of cell 1 cm. The respective temperatures, beginning with the strip nearest the numbered scale, were 20° , 45° , 70° , 90° , 115° , 135° , 155° and 185° . The

part of the spectrogram above $\lambda 4550$ was exposed 40 seconds, while below that wave length the exposure was ten minutes. The apparent band extending entirely across the spectrogram near $\lambda 4550$ is the edge of the screen used in making the long exposure on the violet end of the spectrogram, and must not be confused with an absorption band.

Absorption bands $\lambda 4175$ and $\lambda 4325$ have their centers shifted towards the red end of the spectrum about 25 Å.U. The red edges of bands $\lambda 4325$ and $\lambda 4550$ shade rapidly toward the red. The well marked band $\lambda 4750$ remains unchanged throughout the spectrogram.

The encroachment of the general absorption in the ultraviolet towards the red causes band $\lambda 3625$ to disappear above the fourth strip while band $\lambda 3750$ is scarcely visible above Strip 5. All bands below $\lambda 4500$ become very diffuse as the temperature is raised, and at the highest temperature are hardly more than a single broad hazy absorption band, extending from $\lambda 4000$ to $\lambda 4400$.

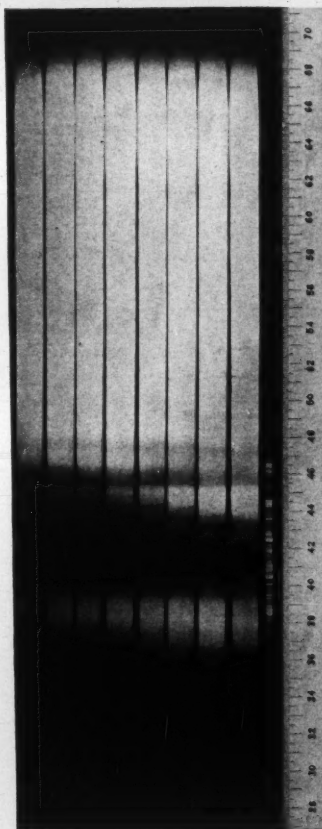
Section *B* is the spectrum of a 0.02 normal solution of uranyl sulphate, the depth of absorbing layer being 10 cm. The respective temperatures, beginning with the strip nearest the numbered scale, were 20° , 45° , 70° , 95° , 115° , 140° and 165° . The exposures were eight seconds in the visible part of the spectrum and an additional exposure of four minutes to the ultraviolet.

The same changes described in *A* take place here, i. e., a strong general absorption in the ultraviolet beyond $\lambda 3500$, and increasing toward the red as the temperature is raised. The most marked widening is in bands $\lambda 4100$, $\lambda 4200$ and $\lambda 4350$. Each of these bands has its center shifted slightly toward the red. Such is also the case with the red edge of band $\lambda 4600$. The $\lambda 4750$ band remains fixed throughout the spectrogram. The very broad hazy bands around $\lambda 5100$, $\lambda 5600$ and $\lambda 6200$ appear and are not appreciably affected by changes in temperature.

THE EFFECT OF DILUTION ON THE ABSORPTION OF LIGHT BY SOLUTIONS

The question as to the effect of dilution on the power of solu-

A



B

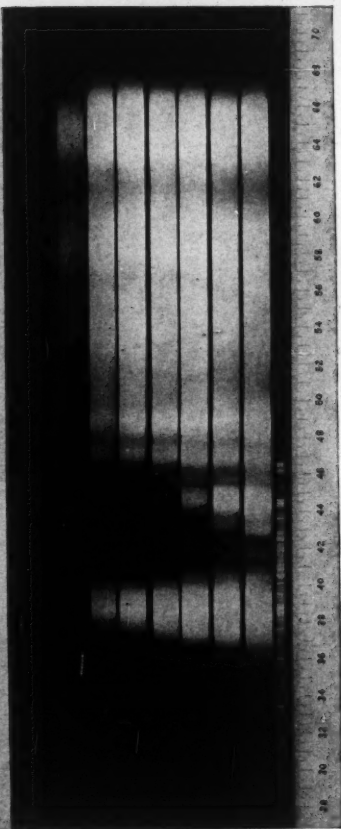


Plate VII

tions to absorb light is an old one. This question became especially prominent at the time the theory of electrolytic dissociation was proposed. In dilute solutions of electrolytes there are practically only ions present, very few molecules existing as such. All of the properties of such solutions are the properties of the ions contained in them. Therefore, the power of these solutions to absorb light must be due to the ions present in them. This was the reasoning in vogue, and the conclusion drawn.

It was at the same time freely recognized that molecules in solution have the power to absorb light. This was shown by the fact that solutions of nonelectrolytes, or completely unionized substances, are often colored; and color in solution means selective absorption of light.

The result of the conclusion drawn from the theory of electrolytic dissociation was that an enormous amount of work was done on the absorption spectra of dilute solutions of both electrolytes and nonelectrolytes. Ostwald carried out an elaborate investigation on the relation between color and dissociation, and published the work under the title "*Ueber die Farbe der Ionen.*"¹ A large number of salts were brought within the scope of this investigation: Salts of an acid having a colored anion, with colorless cations. This is illustrated by the various permanganates, hydrogen, sodium, ammonium, magnesium, zinc, cadmium, etc. Ostwald showed that these salts of any given acid had essentially the same spectra. In a similar manner he studied salts of fluorescein, eosin, iodo eosin, rosolic acid, diazo resorcinol, etc. Ostwald then reversed the process and compared the salts of a given colored base with colorless acids. Thus, he studied the salts of *p*-rosaniline with acetic, chloric, benzoic, hydrochloric, nitric, butyric, salicylic, lactic, etc., acids, and found practically the same absorption spectra for all of these salts.

From the standpoint from which he undertook his investigation, Ostwald may be said to have solved the problem of the rôle of ions in the absorption of light, as far as that could be done with the prism spectroscope.

¹ Z. physik. Chem., 9, 579 (1892).

The problem that we studied was of a different nature. It had to do with the absorption spectra of ions relative to that of the molecules from which they were formed. Some earlier work of Jones and Anderson¹ had shown that if molecules have different action on light from ions, the difference is slight. Indeed, so slight that there would be no hope of detecting it by ordinary means, even with a grating spectroscope. This problem was attacked in the following manner:

Making a Dilution Spectrogram

Before entering upon a detailed discussion of the spectrograms it is wise to state briefly the method used in making any given spectrogram. Throughout all the work done on the effect of high dilution on absorption spectra, under the conditions of Beer's Law, only three exposures were made for any given spectrogram, i. e., only three dilutions were compared. The depths of cell in all cases were 0.5 cm., 50 cm. and 250 cm., the dilution being increased one hundred times between the first two solutions and five times between the last two, or a total dilution of five hundred times between the first and last solution. Smaller depths of cell than five mm. were not used on account of the large percentage error in measuring such depths.

Much difficulty was experienced in getting sufficient light through the longer cells to fill the grating completely, nor was this possible unless the tube containing the solution was constantly moved backwards and forwards so that the image of the source of light was moved along the slit of the camera.

By such a procedure the surface of the grating could be illuminated fairly uniformly, and the exposures gave good results on the photographic plate as is shown by the spectrograms.

In order to insure complete illumination of the grating a uniform procedure was adopted. The longest cell, containing the most dilute solution, was first placed in position, the light passed through and the image of the Nernst glower sharply focused on the slit of the camera in such a manner as to throw

¹ Carnegie Institution of Washington, Publication 110.

as much light as possible on the grating. By holding the eye in the position later to be occupied by the photographic plate, we could easily tell when the grating was properly illuminated.

After everything was properly adjusted the lights were extinguished and the plate inserted in the camera. Great care was taken not to move any parts of the apparatus, the camera was closed, the source of light again turned on, and the exposure made. It is clearly seen that in making any spectrogram, using three cells differing in length so markedly, we virtually had three different sources of light, and, consequently, the length of exposure sufficient to give comparable results on the photographic plate had to be determined by a long series of experiments. In the case of the longest cell, exposures as long as several minutes were made, while with the shortest cell only a few seconds were necessary to give good clear spectrograms on the photographic plate.

The remaining procedure was essentially the same as that described by Jones and Anderson¹ and by other workers in this laboratory.

Neodymium Chloride in Water (see Plate VIII)

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the spark spectrum, were 2.05, 0.0205 and 0.00401 normal, respectively, the corresponding depths of absorbing layer being 0.5 cm., 50 cm. and 250 cm.

For B the concentrations used were 1.025, 0.01025 and 0.00205 normal. The depths of layer were the same as used in A. It is seen that the dilutions are just one-half that of the corresponding layers in A.

The concentrations of solutions used in making C were just half of those in B, i. e., 0.512, 0.00512 and 0.00102 normal. In the entire plate, as in all the dilution work, the most dilute solution is always nearest the spark spectrum.

Since very much of the finer detail and several of the narrowest bands are lost in reproducing and printing the films,

¹ Carnegie Institution of Washington, Publication 110.

our discussion is always based upon the original photographic film. Lines will frequently be discussed which do not appear on the printed plates, but which are very clear and distinct on the photographic film.

A study of *A* shows complete absorption in the violet up to $\lambda 3350$; then slight transmission for about 50 Å.U. The faint hazy band $\lambda 3400$ and the well defined band $\lambda 3450$ – $\lambda 3600$ are not affected by the change in dilution. Hazy bands appear at $\lambda 3820$, $\lambda 4040$ and $\lambda 4200$. Their intensities do not seem to be affected by dilution. The beautiful sharp band $\lambda 4275$ is slightly more intense in the most concentrated solution. The effect of dilution, if any, on the bands $\lambda 4325$, $\lambda 4440$, $\lambda 4600$, $\lambda 4690$, $\lambda 4750$, $\lambda 4820$ is not measurable. On the original film they appear slightly broader, but not more intense, on the third strip.

Bands which have their centers near $\lambda 5100$, $\lambda 5200$ and $\lambda 5800$ are decidedly affected by dilution, the former two appearing distinctly as independent bands in the most dilute solution, diffuse with a single broad band with the center near $\lambda 5150$. There is the greatest change between the second and third strips (in discussing any plate Strip 1 is always nearest the spark lines). The broadening of these bands, both of which have rather hazy edges, is fairly uniform, i. e., they widen both towards the red and violet ends of the spectrum.

The intense band which extends from $\lambda 5690$ to $\lambda 5850$ is affected very markedly by dilution, the widening being almost entirely towards the red end of the spectrum. The violet edge is hardly affected while the widening toward the red is about 50 Å.U. Here also the change in the width of the band is greatest where the change in concentration of the solution is greatest. There is a very faint band, $\lambda 6225$, which appears slightly more diffuse in the most concentrated solution.

The concentrations of the solutions used in *B* are just one-half those of *A*, and it is seen that some of the smaller bands are lost while the broader ones have split into two or more smaller bands. In this film bands near $\lambda 3425$, $\lambda 3475$, $\lambda 3520$, $\lambda 3575$, $\lambda 4275$, $\lambda 4340$, $\lambda 4450$, $\lambda 4700$, $\lambda 4750$, $\lambda 4820$, $\lambda 5100$, $\lambda 5120$, show no change with dilution. The broad band $\lambda 5700$ – $\lambda 5825$

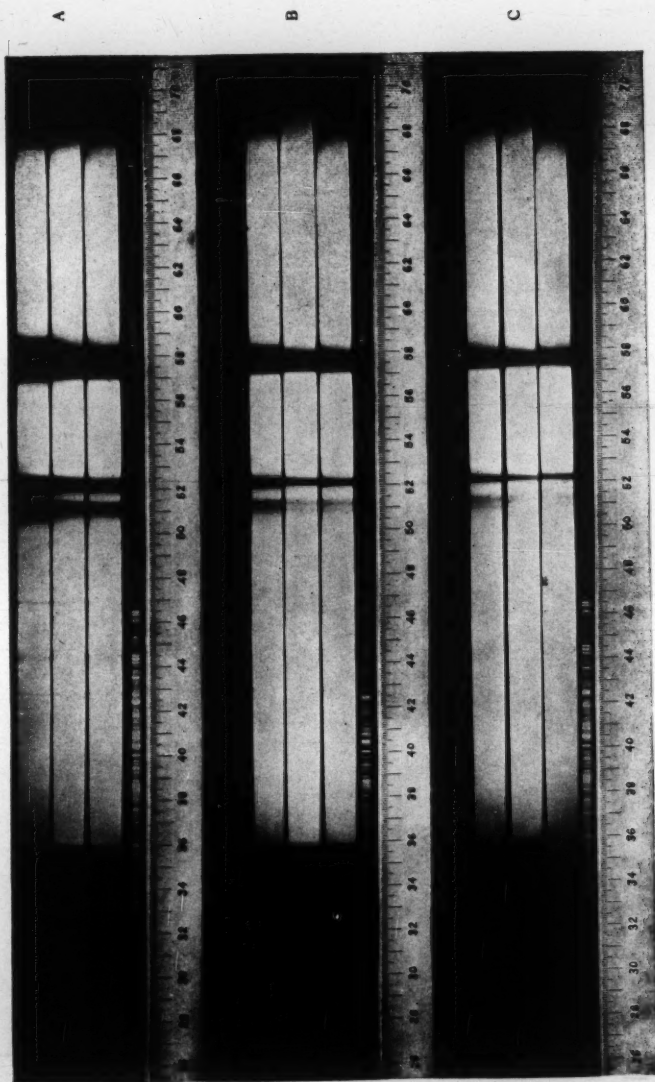


Plate VIII

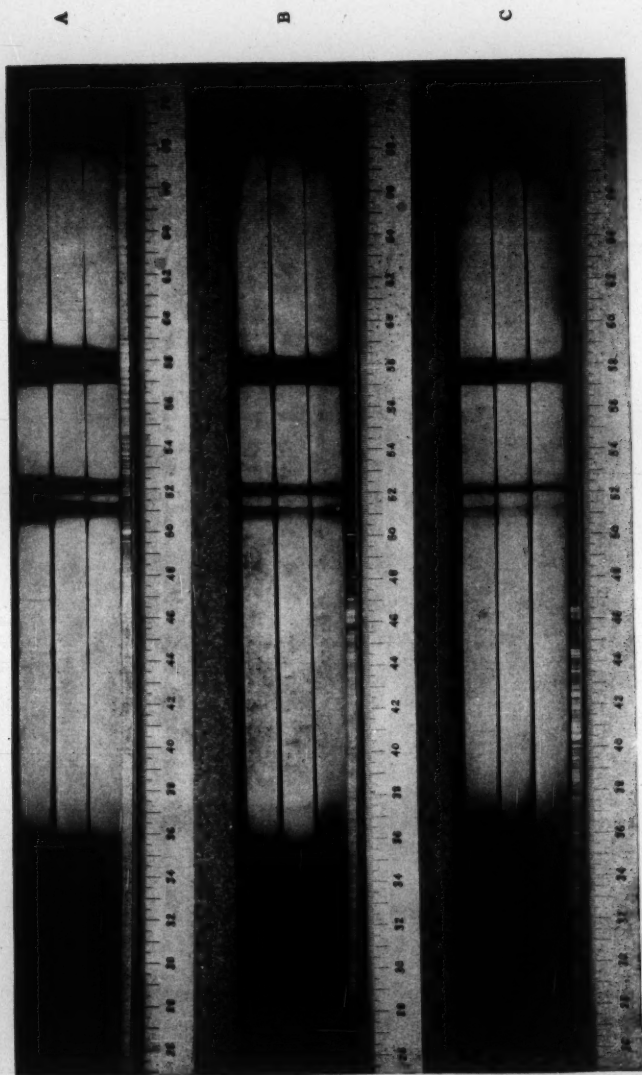


Plate IX

shows a widening of about 25 Å.U., being the only band which is changed by dilution.

C of this plate is the spectrogram of solutions twice as dilute as those of B. No band on this plate shows any appreciable change produced by dilution, except probably a slight widening of $\lambda 5750$.

We then see, from a study of this plate, that in A bands $\lambda 4270$, $\lambda 5100$, $\lambda 5200$ and $\lambda 5750$ narrow with dilution, the amount of change being in the order given; that is, least in $\lambda 5100$ and greatest in $\lambda 5700$. In B there is an appreciable change in only $\lambda 5750$, while in C none of the bands are affected by dilution.

Neodymium Bromide in Water (see Plate IX)

The concentrations of the solutions used in making Negative A, beginning with the solution whose spectrum is farthest from the scale, were 1.66, 0.0166 and 0.0033 normal; the corresponding depths of absorption layer were 0.5 cm., 50 cm. and 250 cm., respectively.

The concentrations used in making B were half of those of A, and those of C half those of B. The same range of cell depth was used in all three sections of this plate, viz., 0.5 cm., 50 cm. and 250 cm., respectively, beginning with the strip farthest from the spark lines. In A characteristic absorption bands appear at $\lambda 3400$, $\lambda 3525$, $\lambda 3800$, $\lambda 4275$, $\lambda 4450$, $\lambda 4700$, $\lambda 4750$, $\lambda 4800$, which are hardly affected by change in dilution, except for a slight increase in the intensity of band $\lambda 4275$ in the most concentrated solution.

The three bands, $\lambda 5090$, $\lambda 5120$ and $\lambda 5210$, narrow uniformly with dilution, the greatest change being between Strips 2 and 3, where the change in dilution is the greatest. With the bromide, as is seen in Plate IX, which gives the spectrogram of neodymium chloride, the effect of dilution is most pronounced in band $\lambda 5750$. The shading is almost exclusively toward the red, the violet edge remaining practically unchanged. This edge shows no change between Strips 1 and 2, yet the red edge is widened as much as 30 Å.U.

In B, where the concentrations were 0.83, 0.0083 and 0.00166 normal, respectively, the depths of absorbing layer

were the same as used in A. There is no measurable change in any of the absorption bands except the band whose center is near $\lambda 4800$. This band shows the characteristic narrowing with dilution, as the dilution is increased. The total change is not greater than 20 Å.U. Band $\lambda 5200$ is slightly more intense in the third strip.

When we reach the dilution used in C, which is four times that of A, any change due to dilution has disappeared except a narrowing of probably 10 Å.U. between the third and second strips.

Taking Plate IX as a whole we see, first, the narrowing due to increased dilution is most marked in A, less in B, and least in C. This is seen to be the same order as their respective concentrations. Considering an individual section, we find the most pronounced narrowing where the change in dilution is greatest—that is, between Strips 2 and 3.

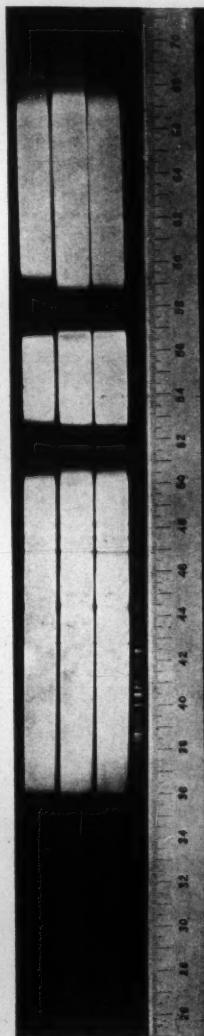
Neodymium Nitrate in Water (see Plate X)

The concentrations of neodymium nitrate used in making Negative A of this plate, beginning with the strip farthest from the numbered scale, were 2.15, 0.0215 and 0.00430 normal, the corresponding depths of absorbing layer being 0.5 cm., 50 cm. and 250 cm., respectively.

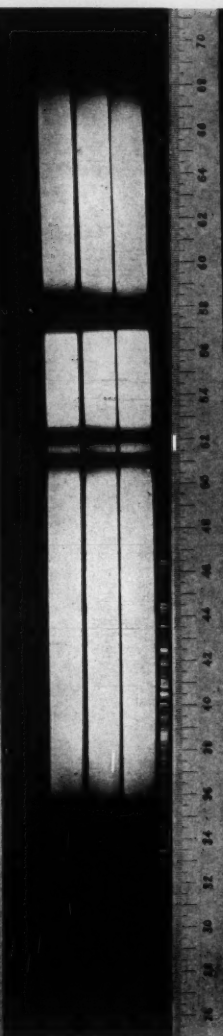
In discussing the absorption bands of this, as well as other plates throughout this paper, we do not attempt to give the exact position of the band in question as has previously been done by many workers; but we simply indicate the position of the band by selecting a wave length near its center. For instance, in speaking of band $\lambda 5800$, we mean that broad band extending from $\lambda 5700$ to $\lambda 5850$. This is not confusing and saves space and time in the description of any plate.

This is probably the best plate we have illustrating the effect caused by dilution. Bands that are hardly affected over the range of dilution given in A are located at $\lambda 3525$, $\lambda 3820$, $\lambda 4440$, $\lambda 4620$, $\lambda 4750$, $\lambda 4830$. The well defined band $\lambda 4275$ is more diffuse, though probably not so intense, in Strip 3. This is in keeping with the behavior of this same band as shown by other salts of neodymium, though probably a little

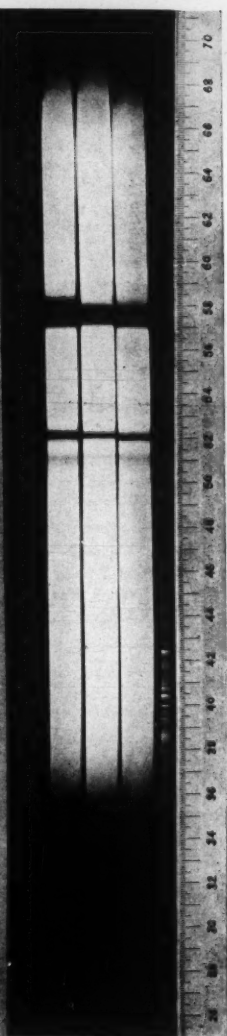
A



B



C



more marked. There is faint transmission at $\lambda 5100$ for about 10 Å.U. In Strip 3, representing the most concentrated solution, the bands $\lambda 5090$ and $\lambda 5125$ have so broadened that they became one band. The $\lambda 5220$ band widens uniformly toward the red and violet as the solution becomes more concentrated.

Band $\lambda 5800$, which is most affected by dilution, shows a total change of probably as much as 70 Å.U., the shading being largely towards the red. In Strips 1 and 2 the violet edge is hardly changed while in Strip 3 it is probably shifted 20 Å.U. On the original film these three strips show absolutely the same development, hence are directly comparable.

Section *B* represents the absorption of neodymium nitrate; beginning with the strip farthest from the numbered scale, the concentrations are 1.075, 0.01075 and 0.00215 normal, the corresponding depths of cell being the same as in *A*. In this section only a few bands need be discussed. Bands $\lambda 5090$ and $\lambda 5125$, which appear as distinct bands in Strips 1 and 2, have slightly broadened so as to form a single hazy band whose center is near $\lambda 5120$. The $\lambda 5750$ band narrows as much as 40 Å.U., almost the entire change being between Strips 2 and 3.

In *C*, the $\lambda 5750$ band alone is noticeably changed, narrowing about 20 Å.U. from Strip 3 to Strip 2, but is not changed in the last dilution, i. e., from Strips 2 to 1.

Neodymium Acetate in Water (see Plate XI)

The concentrations of solutions used in making *A* of this plate were saturated, one-hundredth saturated, and five-hundredth saturated, the corresponding depths of cell being 0.5 cm., 50 cm. and 250 cm., respectively. The most dilute solution is nearest the numbered scale.

This plate was made with very long exposures to see if the apparent widening of the bands could be due to the difference in the amounts of light falling upon the photographic plate. In such a procedure the most concentrated solution was given the longest exposure and yet had the broader bands. It is possible to narrow any given absorption band by length-

ening the time of exposure, but this cannot account for so large a difference as is shown by Strip 3 of Section A. Even in this section it is seen that the third strip has wider bands than either of the other two strips of this section, notwithstanding the fact that the actual exposure of the strip is greater. Thus we see that the difference of exposure cannot account for the changes in the width of bands such as we have noted.

In Section A the violet group of bands in the region $\lambda 3500$ came out beautifully. Such is only the case when quite a long exposure is made. Indeed, in order to show these lines well the exposure must be long enough to destroy those fine, sharp lines in the region of $\lambda 3800$ to $\lambda 4600$. Hence, in this plate the latter group of lines do not appear distinctly, though traces of them can be seen on the original film.

The hazy bands $\lambda 3300$ and $\lambda 3400$ appear on this plate and remain unchanged by dilution.

The three bands, $\lambda 3460$, $\lambda 3500$ and $\lambda 3540$, remain perfectly constant throughout the section. Band $\lambda 5120$, which appears broad and diffuse, shows no change. Band $\lambda 5210$ narrows about 10 Å.U. from the third to the second strip and remains unchanged with the next dilution. The broad band $\lambda 5750$ narrows about 40 Å.U. from the third to the second strips, and about 15 Å.U. with the next dilution.

The concentrations used in *B* were again just half those in *A*, the most concentrated solution being one-half saturated, with succeeding dilutions of one hundred and five times, respectively; the depths of cell, beginning with the strip farthest removed from the scale, were 0.5 cm., 50 cm. and 250 cm.

Again, only bands $\lambda 5220$ and $\lambda 5750$ are changed, but with the acetate the change extends farther with the more dilute solutions. In a word, the narrowing of the bands with dilution is more marked in *B* and *C* than in the case of the chloride, bromide and nitrate. The group of bands near $\lambda 3500$ is not altered with dilution.

The concentrations used in *C* are again half of those in *B*, and the corresponding depths of cell the same as used throughout this plate. Their respective sequence is the same. In this spectrogram only band $\lambda 5750$ changes, and, indeed, this

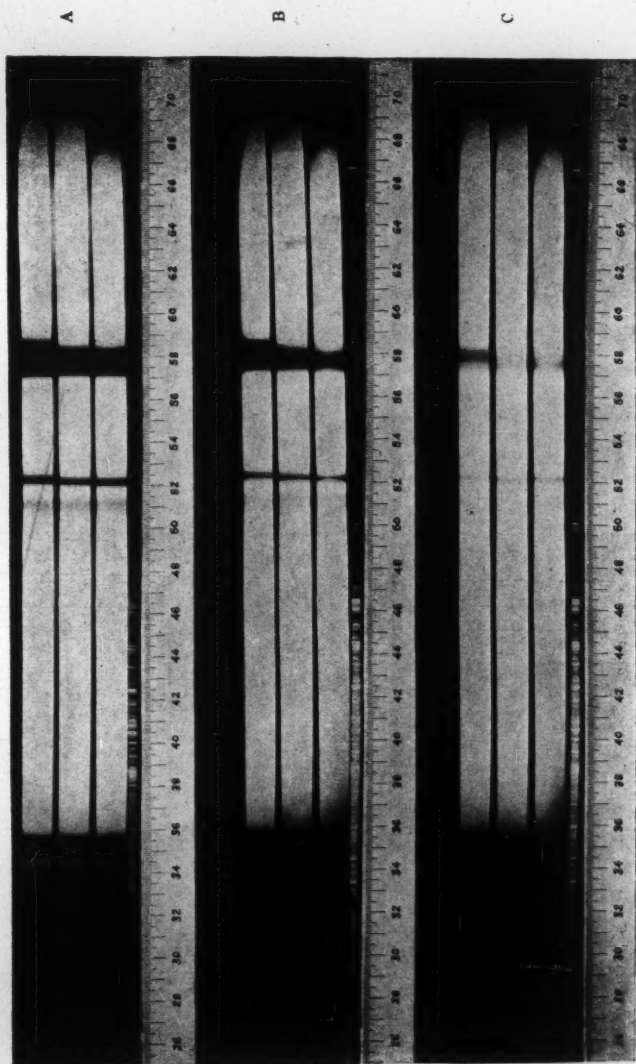
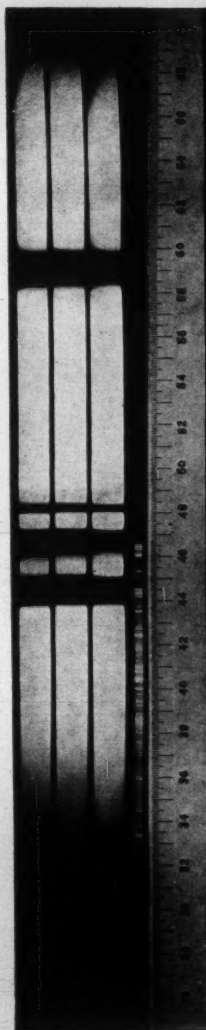


Plate XI

A



B



C

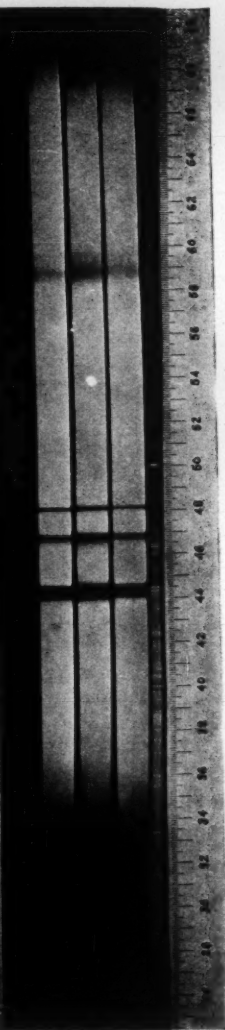


Plate XII

is the only salt of neodymium with which a change with dilution has been noted in so dilute a solution. This band narrows about 20 Å.U.

Neodymium acetate, being the salt of a weak acid, is of course less dissociated at any given concentration than a salt of a strong acid. This salt approaches complete dissociation much more slowly than the others studied. Spectrograms A, B and C show also that the changes caused by dilution are more marked and extend into more dilute solutions than with the chloride, bromide or nitrate. In a word, the changes in the absorption bands due to dilution seem to follow the change in dissociation, that is, they are a direct function of the number of molecules present.

Praseodymium Chloride in Water (see Plate XII)

The concentrations of solutions used in making A, beginning with the strip farthest removed from the numbered scale, were 2.56, 0.0256 and 0.00512 normal, the corresponding depths of absorbing layer being 0.5 cm., 50 cm. and 250 cm., respectively.

The absorption is complete in the ultraviolet up to about $\lambda 3100$. The bands of praseodymium are for the most part broad and have well defined, sharp edges. The violet edge of band $\lambda 4450$ is very sharp and unchanged by dilution, while the hazy red edge is hardly affected. Band $\lambda 4675$ narrows towards the violet about 20 Å.U. while band $\lambda 4830$ is entirely unchanged. The broad band $\lambda 5900$, with slightly hazy edges, shows a total narrowing of about 25 Å.U.

The concentrations of B and C, beginning with the strips farthest from the numbered scale, are 1.28, 0.0128 and 0.00256 normal and 0.64, 0.0064 and 0.00128 normal, respectively. The corresponding depths of absorbing layer were the same as in A. None of the bands are affected by dilution, and we may say that Beer's Law holds very well for praseodymium chloride except for bands $\lambda 4650$ and $\lambda 5900$ in the most concentrated solutions. Even here the change is very slight and not to be compared with corresponding changes with dilution in salts of neodymium.

THE ABSORPTION SPECTRA OF AQUEOUS SOLUTIONS OF CERTAIN
SALTS OF NEODYMIUM AS STUDIED BY MEANS OF THE
RADIOMICROMETER

The radiomicrometer is simply a thermoelement attached to a loop of thin copper wire suspended in a magnetic field. One of the greatest difficulties in constructing this element is to obtain copper wire which is free from all magnetic metals. If perfectly pure copper wire could be found an instrument could be constructed of almost any desired sensibility.

A very good specimen of small copper wire was furnished us by Leeds and Northrup, of Philadelphia. This wire was dipped in dilute nitric acid and the exterior dissolved away until the wire was of proper size. The removal of the outside coating of the wire removed practically all of the magnetic material from it, this material probably being iron from the dies through which the wire was drawn.

It was not a simple matter to construct a satisfactory thermoelectric junction. The alloys used in making this junction were ninety parts bismuth and ten parts tin and ninety-seven parts bismuth and three parts antimony. The method of making the thermoelectric junction, and of soldering it on to the ends of the loop of copper wire, we owe to Professor A. H. Pfund.¹ Fine strips of the alloys were obtained in the following manner:

A few grams of the alloy in question were fused in a vessel free from all magnetic material, and then thrown tangentially upon a clean and smooth glass plate. In this way strips of the metal were obtained of almost any desired thickness. Some were too thin to handle, those used being about 1 mm. wide, 0.01 mm. thick and about 5 mm. in length.

The thermoelement was made by soldering an end of a strip of one of the above-named alloys to an end of a strip of the other, the whole having the form of a letter V. The two free ends of the V were soldered to the two ends of the loop of copper wire. The soldered surfaces were blackened to absorb the energy more completely. At the end of the loop of copper wire opposite the thermoelement a light glass rod is fastened.

¹ *Physic. Rev.*, **34**, 228 (1912). *Physik. Z.*, **13**, 870 (1912).

This carries the mirror and is suspended from above by a quartz fiber. The mirror employed was about 4 square mm. This entire system, consisting of thermoelement, loop of copper wire and mirror, weighed about twenty milligrams. It was suspended by means of a quartz fiber so that the loop hung between the poles of a strong magnet. This entire system was suspended in the interior of a glass tube, the tube being closed by a ground glass stopper, and provided with suitable windows for exposing the junction and observing the mirror. The upright tube was provided with a side tube for evacuation, and by a method devised by Professor Pfund a very high vacuum could be obtained and maintained for any desired length of time. By suitably turning the ground glass stopper in the top of the glass tube, the loop of copper wire, mirror, and, indeed, the whole system could be made to occupy any position relative to the magnets, even after the entire system had been evacuated. The whole apparatus was supported upon a leveling stand and packed in cotton to protect it from external radiation, the thermal junction alone being exposed to the radiation in question.

The sensibility of the instrument used can be seen from the following data: It had a full period of 8 seconds, and with a candle at a distance of a meter gave a deflection of 15 cm., when the light was allowed to fall on the junction after passing through a glass window.

When the apparatus was pumped out and the radiomicrometer thus suspended in a vacuum the deflection for a candle at a distance of a meter was 50 cm. Since glass absorbs just about half the energy emitted by a candle, our radiomicrometer, when provided with a rock salt window and exposed to a candle at a distance of a meter, would give a deflection of about 100 cm.

How our instrument compared with the radiomicrometers constructed and used by other investigators can be seen from the following table, taken in part from the paper by Coblentz:¹

¹ Bull. Bur. Standards, 4, No. 3.

	Whole period in seconds	Deflection in cm. per sq. mm. Candle 1 m. distance
Boys ¹	10	0.9
Paschen ²	40	3.0
Lewis ³	20	1.3
Coblentz ⁴	40	3.6
Coblentz ⁴	25	6.0
Jones and Guy	8	8.0
Jones and Guy	7	25.0 (<i>vacuo</i>)
Jones and Guy	7	50.0 (<i>vacuo</i>) rock salt window

The magnetic control due to small amounts of magnetic impurities in the copper wire was, of course, greater the more sensitive the instrument. For this reason the radiomicrometer was not used in a vacuum. The length of the quartz fiber was so chosen that a candle at a distance of a meter gave a deflection of 16 cm. The half period was 4 seconds. This sensibility was found to be quite sufficient for work in the red and infrared, and even for wave lengths as short as 4500 Å.U. The measurement could be carried out quickly and the magnetic disturbance was practically negligible.

When the thermojunction was exposed to the radiation and the source of energy removed, the instrument returned to its original zero position to within 0.5 mm. In most cases several readings were made for a given amount of radiation, and these usually agreed to within one per cent. The source of energy was a Nernst glower attached to a storage battery, the amperage being 1.2 and the voltage 110. This was found to be very constant, successive readings in the same position of the spectra agreeing well with one another.

The vessels used for holding the solutions were made of brass and gold plated. They were about 4 cm. in diameter and of the desired thickness. The ends were made of the best optical glass. Vessels of the same thickness gave practically the same deflection both when empty and when filled with water.

¹ Phil. Trans., (A) 180, 159 (1889).

² Wied. Ann., 48, 275 (1893).

³ Astrophys. J., 2, 1 (1895).

⁴ Bull. Bur. Stand., 1 Sept. (1907).

Method of Procedure

The light from a Nernst glower was rendered parallel by a lens, then passed through the vessel containing the solution and allowed to fall on the slit of a Hilger spectroscope. The solution was first inserted into the path of the light, and then the pure solvent, this being done without disturbing the adjustment. By means of a movable framework, first the vessel containing the solution and then that containing the solvent were interposed in the path of the beam. A metal screen interposed between the Nernst glower and the vessel containing the solution allowed the light to pass through the solution only when an observation was being made. By this means the thermoelectric junction was exposed to the radiation only long enough to read the deflection of the mirror.

The light, after passing through the solution and the slit of the spectroscope, fell upon the prism of the Hilger spectroscope. A second slit was inserted in the spectroscope instead of the eye-piece. The light passed from the prism through this second slit, and was then focused on the thermal junction of the radiomicrometer.

The Hilger spectroscope contained a milled head, graduated so that the wave lengths could be read off directly. By suitably turning this head any desired wave length could be thrown upon the junction of the radiomicrometer.

The width of the slit used in the visible part of the spectrum was 0.4 mm. In the infrared where there is far more energy, the slit width was cut down to 0.22 mm. A series of readings was carried out as follows: The vessel containing the solvent was first placed in the path of the beam of light, the screen removed, and the deflection of the mirror noted. Then the vessel containing the solution was put in the same place that was formerly occupied by the vessel containing the solvent, the screen removed, and the deflection again noted. The prism was then turned slightly by means of the graduated and calibrated head, and a new wave length allowed to fall on the junction. By repeating this procedure any wave length could be allowed to fall on the junction. If we represent by

I the deflection with the solution in the path of the beam of light, and by I_0 the deflection with the solvent in the path of the light beam, the percentage of light which passed through the solution would be represented by I/I_0 . In the following table we have the ratio of I/I_0 for an 0.875 normal solution of neodymium chloride, the length of the layer being 10 mm.:

λ	I/I_0	λ	I/I_0	λ	I/I_0	λ	I/I_0
4860	80	5670	1	6700	60	7720	34
4920	82	5720	0	6720	57	7760	14
4950	61	5770	1	6760	63	7810	4
4990	40	5790	3	6780	61	7860	0
5010	29	5830	11	6810	74	7920	2
5030	13	5850	23	6850	97	7980	6
5050	7	5880	42	6910	99	8020	16
5060	11	5890	63	6990	97	8060	34
5090	13	5920	79	7060	91	8110	59
5130	10	5950	90	7100	80	8180	79
5150	2	5970	92	7140	47	8230	91
5160	4	6000	95	7190	29	8330	95
5180	13	6090	94	7220	8	8360	90
5200	31	6110	92	7240	1	8400	80
5220	45	6140	93	7290	0	8450	62
5250	62	6220	91	7330	0	8500	37
5300	92	6290	94	7370	5	8550	20
5350	94	6380	98	7410	17	8605	16
5440	91	6430	98	7450	42	8660	23
5500	80	6500	99	7500	64	8720	41
5560	69	6570	99	7550	79	8780	43
5590	50	6600	95	7600	84	8890	65
5630	26	6620	91	7650	75	9000	90
5650	9	6660	75	7690	57	9580	100

The above table may be taken as typical of the results obtained with any given salt. When we first began to investigate any given salt we made a preliminary survey of its spectrum, noting the approximate positions of the absorption lines and bands. We then made our observations very close together over the regions in which the preliminary survey had indicated the presence of lines and bands. The number of absorption lines and bands, as is well known, is very great in the case of neodymium compounds, and these lines and bands frequently have very sharp edges. This made the work with

this substance very difficult. The proper width of slit and position had to be chosen or a considerable error would result. Given a slit width which was approximately the same as that of an absorption line, a very slight movement of the slit or prism would change very greatly the total amount of energy falling on the thermal junction.

Take the neodymium band $\lambda 4275$, which is very intense but narrow. On both sides of this band there is a region of almost perfect transparency. If the slit width necessary to give the desired deflection was greater than the width of this band, light would pass through around the edges of the band, and an error, which might be of very considerable magnitude, would result. With substances which did not contain such fine lines and bands the work would be much simpler.

The entire spectrum from wave lengths $\lambda 4000$ to $\lambda 20000$ was observed at intervals of from 20 Å.U. to 50 Å.U., except in the regions where the preliminary survey indicated the absence of absorption lines and bands.

An examination of the preceding table will show at $\lambda 4820$ a transparency of 80 per cent., which rapidly decreases, reaching the first minimum at $\lambda 5050$. There the transparency amounts to only 7 per cent. The transparency then increases a little and quickly drops to 2 per cent. at $\lambda 5150$. The transparency then increases, becoming nearly complete at $\lambda 5350$. We have here, then, a double band with greater absorption on the red side. Other minima appear at $\lambda 5720$, $\lambda 7300$, $\lambda 7860$ and $\lambda 8605$. Bands $\lambda 7300$, $\lambda 7860$ and $\lambda 8605$ do not appear on the photographic plate, and the last two seem never to have been detected before.

The salts of neodymium were studied as far as $\lambda 20000$, but beyond 1μ there seems to be complete transparency. The absorption of water is, as is well known, very great in the region $\lambda 12000$ to $\lambda 20000$.

Discussion of the Results

The results are plotted in the following eleven curves. The abscissae are percentage transparencies, the ordinates are wave lengths. These curves, since they represent the transparen-

cies of the solutions in question, are called *transmission curves*.

Figs. 1, 2 and 3 represent the transparency of solutions of

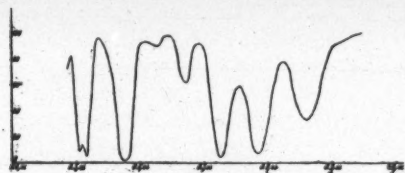


Fig. 1.

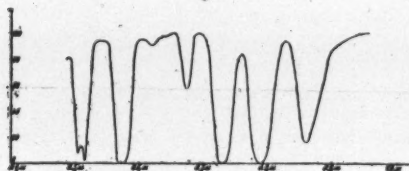


Fig. 2

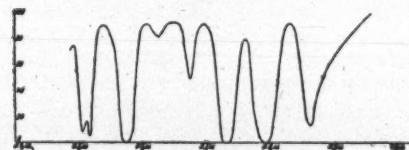


Fig. 3

neodymium chloride expressed in terms of Beer's Law. If we represent the concentration by N and the depth of layer by d ,

$$Nd = \text{constant}$$

The concentration represented in Fig. 1¹ is 3.43 normal, in Fig. 2 0.875 normal, and in Fig. 3 0.472 normal. The depth of layer represented by Fig. 1 is 2.5 mm., by Fig. 2 10 mm., and by Fig. 3 20 mm. The concentration and depth of layer were thus varied so as to keep Nd constant.

¹ Our attention was drawn to the existence of these bands in the infrared by Pfund, who had already mapped them radiometrically for neodymium nitrate.

If the solvent plays no rôle in the absorption, the three sets of curves must fall directly over one another, i. e., be identical, since the number of absorbing parts in the path of the beam of light is kept constant. A comparison of the curve shows that, in general, the more concentrated the solution the less the transparency and the broader the absorption bands. In the more dilute solution the intensity of the bands is greater. This comes out very clearly in the red and infrared region, where there is greater accuracy of measurement.

Take the three absorption bands, $\lambda 7300$, $\lambda 7850$ and $\lambda 8600$. In Curve 1 the minima of these bands are approximately 4, 8, and 33 per cent., while the minima in Curve 2 are much less. In Fig. 2 the bands $\lambda 7300$ and $\lambda 7850$ reach the abscissa, which means that there is no transmission. At this dilution the band $\lambda 8600$ has still considerable transparency, as will be seen by the fact that it remains a considerable distance above the abscissa. The band $\lambda 8600$ does not reach the abscissa even at the dilution represented in Fig. 3.

All of the bands manifest the above phenomena, the change in intensity being greatest where the change in dilution is greatest, i. e., from Curve 1 to Curve 2. With increase in dilution the position of the middle of the band is displaced toward the region of greater wave length.

Similar results were obtained with neodymium bromide, and these are plotted in Curves 4, 5 and 6. The concentrations and depths of layer were varied so that the product of the two remained constant. The work with the bromide was, therefore, done in terms of Beer's Law. The concentrations used were 1.66 normal, 0.415 normal and 0.207 normal, the corresponding depths of the solution being 2.5 mm., 10 mm. and 20 mm. We find here the same general changes in the intensities of the bands as with the chloride. The more dilute the solution the more intense and the narrower the band.

This is shown by comparing Figs. 4, 5 and 6. In Fig. 4, which represents the most concentrated solution of the three, the bands are the least intense. In Fig. 5 the opacity of two of the

bands has become complete, shown by the fact that these touch the abscissa.

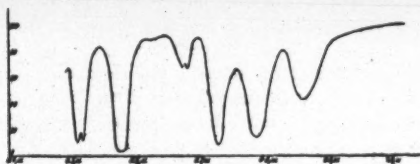


Fig. 4.



Fig. 5.

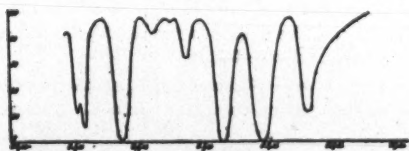


Fig. 6.

Neodymium nitrate was also studied and the results are plotted in Curves 7, 8 and 9. The concentrations used were 2.95, 0.736 and 0.368 normal. The depths of layer were 2.5 mm., 10 mm. and 20 mm.

Band $\lambda 5700$, Curve 7, appears to be an exception to the general relation pointed out above, connecting intensity and width of band with dilution. This was the first band studied by means of the radiomicrometer, and comparatively small deflections were observed in this region of the spectrum. The

remaining bands of neodymium nitrate, however, show the same relations that have been pointed out for the chloride and bromide; with increasing dilution the intensities of the

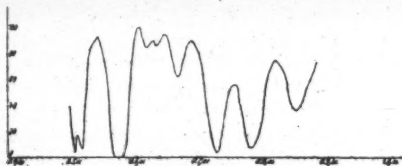


Fig. 7

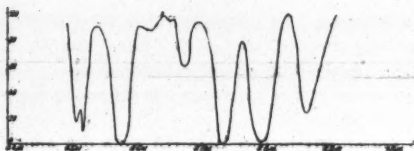


Fig. 8

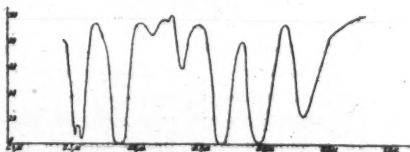


Fig. 9

bands increase and the centers seem to be displaced somewhat towards the longer wave lengths.

We then have three salts, neodymium chloride, neodymium bromide and neodymium nitrate, all of which show a marked increase in the intensity of the absorption bands with increase in dilution, when the product of concentration and depth of layer is kept constant, i. e., when the conditions demanded by Beer's law are fulfilled.

Possible Explanation

It is well known that a resonator vibrates more strongly if

excited by the vibrations for one single vibrating resonator of the same pitch than when set into vibration by a large number of resonators, one of which has the same period as its own, and the others slightly different periods. In other words, if several vibrators are near one another, every one exerts a certain influence on its neighbors. The result is that no one of them has exactly the same period as the original resonator.

The presence of one vibrator seems to exercise a damping influence on the other, and causes it to vibrate with a period slightly different from its normal period. We thus have less perfect resonance.

The absorption of light by solutions appears to be a resonance phenomenon. In a concentrated solution the vibrators are relatively close to one another and mutually affect one another. The result is an imperfect resonance, and, consequently, the absorption bands are less intense in the more concentrated solution.

The vibrators are farther removed from one another in the more dilute solutions, and in most cases are probably surrounded by large amounts of water of hydration. The damping effect would not be so pronounced, and a resonator would have greater freedom to vibrate in its own period. In such cases we would have a more nearly perfect resonance, and the resulting absorption bands would be more intense. This tentative explanation seems to account for the observed facts. Fig. 10 is plotted from the results for neodymium sulphate, and Fig. 11 from those for neodymium acetate. The concentration of the sulphate is 0.118 normal, and of the acetate 0.84 normal. The length of the solution of the sulphate is 10 mm. and of the acetate 2.5 mm.

The absorption of the acetate, for a given concentration, is much greater than that of any other neodymium salt thus far studied. This agrees with the results obtained photographically.

The absorption of water beyond 1μ is very great, as has already been stated. If we are working with very concentrated solutions and use a "water" vessel of the same thickness as the "solution" vessel, it is obvious that the results would

not be comparable. Take the 3.43 normal solution of neodymium chloride, it contains, for a given thickness, only about ninety per cent. as much water as the same thickness of pure water. It is then obvious that in the longer wave lengths

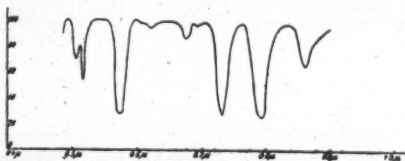


Fig. 10

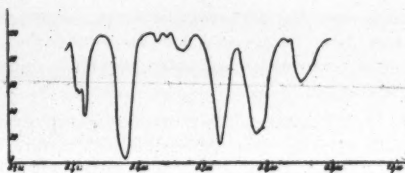


Fig. 11

a correction term must be introduced for this difference. This was practically negligible with salts of neodymium, since these do not seem to have any bands in the region where water has appreciable absorption.

Salts of praseodymium have bands in the infrared, at least as far as 2μ . In such cases the above correction must be introduced. This correction can be introduced in either of two ways. We can take the specific gravity of the solution and from the concentration calculate the amount of water present. We can then use a "water" vessel of suitable thickness. For example, if the very concentrated solution in question contains only 90 per cent. of water, and we use a vessel for the solution which is 10 mm. thick, we must use a vessel for the water which is only 9 mm. thick. In this way the beam of light is made to pass through the same amount of water both in the case of the solution and of the solvent, and the absorption due to water is, therefore, the same in the two cases.

The second method of procedure is to allow the "water" vessel and the "solution" vessel to be of the same thickness, and to apply mathematically the proper correction to the results obtained.

SUMMARY AND GENERAL DISCUSSION OF MOST IMPORTANT RESULTS

Although in the discussion of each plate, there has been given a brief account of the changes and points of special interest, it is thought wise to bring together the most important facts established, and, if possible, try to interpret them.

In the study of the effect of high temperatures on aqueous solutions, it is seen that while certain bands change in intensity, becoming broad or in certain instances actually shifting their positions, yet, other bands are apparently unchanged over a range of 200°.

Plates I, II, III and IV, which are the absorption spectra of neodymium chloride, bromide, nitrate and acetate, respectively, show marked change with rise in temperature in only the two bands λ_{5275} and λ_{5800} . There is a general tendency for almost all the other bands to become slightly more diffuse, although it is difficult to say that this may not be caused by general absorption. However, with bands λ_{4275} and λ_{5800} the change is a real one. Experiments made by overexposing the strips corresponding to the high temperatures had little or no effect on the changes produced by raising the temperature. Since the development of a photographic plate depends upon the amount of light falling upon it, independent of the period of time it is falling, it is clear that the effect of general absorption could be counterbalanced by increased time of exposure.

The two bands mentioned above widened rapidly as the temperature was raised, this widening being, in both cases, almost entirely towards the longer wave lengths.

The band λ_{5800} , in the most concentrated solutions, widened as much as 80 Å.U., while the amount of widening was directly dependent upon the concentration. It is always greater

between the second and third strips. This is what we should expect, since the change in dilution between the two solutions whose spectrogram they represent is one hundred times, while the succeeding dilution was only five times. The violet edge of this band remains almost constant over the range of temperature studied.

The band λ_{4275} , a very sharp, intense band at the lower temperatures, becomes rapidly diffuse as the temperature of any solution is raised. With this band, as with the λ_{5800} band just discussed, the change is taking place almost exclusively on the red edge, the shading being a gradual one. This edge, the definition of which at ordinary temperature could be seen almost to 1 Å.U., covers about 40 Å.U. at 190° . The double band with its center near λ_{5150} remains about constant in any given section, but in those bands whose width or intensity is changed by change in temperature the change is greatest in the most concentrated solutions, i. e., where the number of molecules is greatest.

Salts of praseodymium are only slightly affected by change in temperature. In the most concentrated solutions all the bands are slightly widened, while in the more dilute solutions there is no appreciable change.

In the salts of uranyl studied, it was found that nearly every band widened with rise in temperature, the widening in two instances being rapidly towards the red. Several of the bands seem to have their centers shifted as much as 15 Å.U. towards the red end of the spectrum.

As mentioned in the discussion of the plates, the uranyl bands almost all occur in the ultraviolet end of the spectrum, and in this region the general absorption increases rapidly as temperature rises. On account of this, together with the haziness of all uranyl bands, it is difficult to make exact measurements upon them. It seems evident that in some cases both the width and position of the bands are changed by change in temperature. The change is always a widening of the band in question as the temperature rises.

In the part of this paper which deals with the effect of high dilution, it has been shown that at least three of the neodymium

bands are affected, namely, $\lambda 4275$, $\lambda 5150$ and $\lambda 5800$. Of these three the change is apparently greatest in $\lambda 5800$, next in $\lambda 5150$, and least in $\lambda 4275$. It cannot be said to be really least in $\lambda 4275$ but rather less noticeable. It is probable that the percentage change, with regard to the total width of the band, is much greater with this band than in the two preceding bands.

The change in $\lambda 5800$ is a widening of about 60 Å.U. in the most concentrated solutions, as we pass in the direction of the concentrated solutions. This widening, as in the temperature effect, is entirely towards the red end of the spectrum. The widening of the double band near $\lambda 5150$ is uniform towards both ends of the spectrum. This change is appreciable only in the very concentrated solutions.

Considering a single plate, which represents the spectrogram of three different dilutions, in terms of Beer's Law we see the following:

This change is greatest in Section A, i. e., the most concentrated solution; less in B; and hardly measurable in C.

The change is greater with the acetate than with the other salts of neodymium, and is always greatest where the difference in concentration is greatest, i. e., between Strips 2 and 3.

When we consider the effect of dilution on the dissociation we see it is in this same ratio, i. e., there is a much greater percentage change in the relative number of molecules present in concentrated than in dilute solutions, for a given change in dilution.

In that dilution of any solution where the relative number of molecules is greatest—the association greatest—bands $\lambda 4275$, $\lambda 5150$ and $\lambda 5800$ are widest, and the change in dilution which affects the relative number of molecules to the greatest extent causes the greatest change in the bands. In the more dilute solutions where this change in the number of molecules is small, there is a relatively small change in the width or intensity of the bands.

A rise in temperature produces the same change upon bands $\lambda 4275$ and $\lambda 5800$ as concentrating the solution, that is, rise in temperature and dilution produce the reverse effect. Band

λ_{5100} is changed by dilution and not by temperature. From these facts it seems that band λ_{5100} may be associated with the molecules themselves, while bands λ_{4175} and λ_{5800} have more to do with the hydrated molecule. A rise in temperature would make the hydrated absorbers, or the hydrated system containing the absorbers, simpler, and, therefore, probably freer to respond in resonance to a larger number of wave lengths. This would cause a widening of the absorption bands. Concentrating the solution, i. e., decreasing the actual amount of solvent, would, according to the mass law, decrease the amount of solution, and, hence, have the same effect as raising the temperature. This is exactly what is shown to be the case by the plates with bands λ_{4275} and λ_{5800} .

The λ_{5100} band is not appreciably affected by temperature, but is changed by dilution, being widest in the most concentrated solutions.

Since temperature has little or no effect on this band, it is probable that here hydration plays very little part. Since the band widens as the number of molecules is increased, it seems to be in some way associated with the unhydrated molecules.

So far as can be seen from the photographic plates, the other neodymium bands are affected neither by dilution nor by temperature. The absorbers in this case are probably associated with the neodymium atoms or ions.

DESCRIPTION OF PLATES

- Plate I. A. Neodymium Chloride in Aqueous Solution. Concentration, saturated. Depth of layer, 1 cm. Respective temperatures, 20°, 45°, 70°, 95°, 115°, 140° and 165°, with lowest temperatures nearest spark lines. Exposures made on rising temperature.
- B. The same solution used in Plate A, with exposures made as cell cooled. Depth of layer and concentration the same as Plate A. Temperatures, 165°, 140°, 115°, 95°, 70°, respectively. Highest temperatures nearest spark lines.
- Plate II. A. Neodymium Bromide in Aqueous Solution. Concentration, 1.66 normal. Depth of cell, 1 cm. Respective temperatures, 20°, 45°, 70°, 95°, 120°, 140°, 175°, 190°. Lowest temperature nearest spark spectra.

- B.* Neodymium Bromide in Aqueous Solution. Concentration, 0.166 normal. Depth of cell, 10 cm. Respective temperatures, 20°, 45°, 70°, 95°, 115°, 135°, 155° and 190°. Highest temperature nearest spark spectra.
- Plate III. *A.* Neodymium Nitrate in Aqueous Solution. Concentration, 0.1 saturated. Depth of layer, 10 cm. Temperatures, 20°, 45°, 70°, 95°, 115°, 140°, 165°, 190°. Exposures made as temperature was raised. Lowest temperature nearest spark lines.
- B.* The same solution of neodymium nitrate as used in Plate A. Concentration and depth of layer identical with A. Temperatures, 190°, 165°, 140°, 115°, 95°, 70°, 45° and 20°. Exposures made on falling temperatures. Highest temperature nearest spark lines.
- Plate IV. *A.* Neodymium Acetate in Water. Concentration, 0.1 saturated. Depth of cell, 10 cm. Trace of acetic acid added to prevent precipitation. Temperatures, 20°, 45°, 70°, 95°, 120°, 140°, 160° and 190°. Exposures made on rising temperature. Lowest temperature nearest spark line.
- B.* Solution, depth of cell and concentration the same as A. Temperatures, 190°, 165°, 145°, 125°, 100°, 75°, 50° and 25°. Exposures made on falling temperatures.
- Plate V. *A.* Praseodymium Nitrate in Water. Concentration, 2.6 normal. Cell depth, 1 cm. Temperatures, 12°, 32°, 52°, 72°, 92°, 112°, 125° and 145°. Lowest temperature nearest spark lines.
- B.* Praseodymium Nitrate in Water. Concentration, 0.26 normal. Cell depth, 10 cm. Temperatures, 20°, 45°, 70°, 95°, 115°, 135° and 165°. Lowest temperature nearest spark lines.
- Plate VI. *A.* Uranyl Nitrate in Water. Concentration, 0.2 normal. Cell depth, 1 cm. Temperatures, starting with strip nearest spark lines, were 20°, 40°, 60°, 80°, 100° and 120°, respectively.
- B.* Uranyl Nitrate in Water. Concentration, 0.02 normal. Depth of cell, 10 cm. Temperatures, starting with exposure nearest spark lines, were 20°, 45°, 70°, 95°, 115°, 140° and 165°, respectively.
- Plate VII. *A.* Uranyl Sulphate in Water. Concentration 0.166 normal. Depth of cell, 1 cm. Temperatures, beginning nearest spark lines, 20°, 45°, 70°, 95°, 115°, 135°, 155° and 185°, respectively.
- B.* Uranyl Sulphate in Water. Concentration, 0.2 normal. Cell depth, 10 cm. Respective temperatures, beginning nearest spark lines, were 20°, 45°, 70°, 95°, 115°, 140° and 165°.

- Plate VIII. A. Neodymium Chloride in Water. Concentrations, 2.05, 0.0205 and 0.00401 normal. Respective depths of cell, 0.5 cm., 50 cm. and 250 cm. Most dilute solution nearest spark lines.
- B. Neodymium Chloride in Water. Concentrations, 1.025, 0.01025 and 0.00205 normal. Depths of cell, starting with strip farthest from spark lines, were 0.5 cm., 50 cm. and 250 cm., respectively.
- C. Neodymium Chloride in Water. Concentrations, 0.512, 0.00512 and 0.00102 normal. Depths of cell, beginning with strip farthest removed from spark lines, were 0.5 cm., 50 cm. and 250 cm., respectively.
- Plate IX. A. Neodymium Bromide in Water. Concentrations, 1.66, 0.0166 and 0.0033 normal. Corresponding depths of cell, 0.5 cm., 50 cm. and 250 cm., respectively. Most dilute solution nearest spark lines.
- B. Neodymium Bromide in Water. Concentrations, 0.83, 0.0083 and 0.00166 normal. Corresponding depths of cell, 0.5 cm., 50 cm. and 250 cm., respectively. Most dilute solution nearest spark lines.
- C. Neodymium Bromide in Water. Concentrations, 0.415, 0.00415 and 0.00083 normal. Corresponding depths of cell, 0.5 cm., 50 cm. and 250 cm., respectively.
- Plate X. A. Neodymium Nitrate in Water. Concentrations, 2.15, 0.0215 and 0.00430 normal, respectively. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm., respectively. Most dilute solutions nearest spark lines.
- B. Neodymium Nitrate in Water. Concentrations, 1.075, 0.01075 and 0.00215 normal. Corresponding cell depths were 0.5 cm., 50 cm. and 250 cm., respectively.
- C. Neodymium Nitrate in Water. Concentrations, 0.537, 0.00537 and 0.00107. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm., respectively. Most dilute solutions nearest spark lines.
- Plate XI. A. Neodymium Acetate in Water. Concentrations, saturated, 0.01*s* and 0.002*s*, where *s* represents a saturated solution of the salt in water at 25°. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm., respectively.
- B. Neodymium Acetate in Water. Concentrations, 0.25*s*, 0.005*s* and 0.001*s* (*s* being a saturated solution as above). Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm.
- C. Neodymium Acetate in Water. Concentrations, 0.25*s*, 0.0025*s* and 0.0005*s*. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm., respectively.

- Plate XII. A. Praseodymium Chloride in Water. Concentrations, 2.56, 0.0256 and 0.00512 normal, respectively. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm.
- B. Praseodymium Chloride in Water. Concentrations, 1.28, 0.0128 and 0.00256 normal. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm., respectively.
- C. Praseodymium Chloride in Water. Concentrations, 0.64, 0.0064 and 0.00128 normal. Corresponding depths of cell were 0.5 cm., 50 cm. and 250 cm., respectively.

[Contributions from the Chemical Laboratory of Harvard College]

IODTRIBROMNITROBENZENE

BY C. LORING JACKSON AND WEBSTER N. JONES

The 2,4,6-tribrom-3-nitraniline, which formed the starting point of this research, melts according to Körner¹ at 102°.5, according to Remmers² at 214°–215°; it was obvious, therefore, that a study of this substance was necessary before we could begin the work which we had undertaken. Körner prepared his product by the action of bromine vapor on *m*-nitraniline, and on repeating his work we obtained exactly the same results (except that our product melted at 101°.5 instead of 102°.5 as given by Körner), and in this we agree with Nölting and Collins³ and Bentley⁴, who also repeated Körner's work. Bentley also tried to follow the method of Remmers, the action of nitric acid on tribromacetanilide, but did not succeed in finding the conditions for the formation of the tribromnitracetanilide, obtaining instead tetrabrombenzene, dinitrodibrommethane, bromanil, oxalic acid and picric acid. After some trouble we found the conditions under which the tribromacetanilide was converted into tribromnitracetanilide, which consisted in heating on the steam bath until the first brown fumes appeared, that is, for less than a minute. Longer action gave a mixture similar to that described by Bentley, from which we isolated bromanil, and un-

¹ Gazz. chim. ital., 1874, 348.

² Ber. d. chem. Ges., 7, 351 (1874).

³ Z. Chem., 1876, 347.

⁴ THIS JOURNAL, 20, 472 (1898).

doubtedly should have detected his other products if we had studied this reaction as carefully as he did, but it lay outside of the limits of our research. The 2,4,6-tribrom-3-nitroacetanilide melts at 208°-209°. Remmers does not mention his melting point. When boiled for 5 hours with sulphuric acid of specific gravity 1.44, this substance was converted into Körner's tribromnitraniline melting at 101°. Remmers' tribromnitraniline melting at 214°-215°, therefore, does not exist. He found great difficulty in saponifying his acetanilide, neither sodic hydroxide nor hydrochloric acid producing any effect upon it; finally he thought he had achieved the desired result by heating in a sealed tube with aqueous ammoniac hydroxide. This and the higher melting point suggest that his substance may have been the unaltered acetanilide, and that he was misled by a bad analysis.

The 2,4,6-tribrom-3-nitrodiacetanilide of Remmers melts at 168°-169°, and is evidently the substance with this melting point described by H. L. Wheeler¹ as the monacetanilide. This latter substance ($C_6HBr_3NO_2 \cdot NHC_2H_5O$) melts at 208°-209°, as already stated.

The 1-iod-2,4,6-tribrom-3-nitrobenzene melts at 144°-145°; it reacts at ordinary temperatures with an alcoholic solution of sodic ethylate, giving a mixture of the bromide, iodide and nitrite of sodium and organic products, from which we isolated an ioddibromnitrophenetole melting at 121°. The other compounds, which must have been formed, appeared in such an oily state that we were unable to obtain any of them pure in the time at our disposal.

The substances 2,4,6-tribrom-3-nitraniline, 2,4,6-tribrom-3-nitrobenzene, 2,4,6-tribrom-1-iod-3-nitrobenzene and 2,4,6-tribrom-1,3-dinitrobenzene seemed well adapted for the study of the effects of different radicals on the ease with which the bromine can be replaced, and we had even intended to make quantitative studies of the progress of such replacements, but we were obliged to abandon this plan as far as the nitraniline was concerned, because its rate of action was so much slower than those of any of the other substances, and

¹ THIS JOURNAL, 17, 702 (1895).

also because the amorphous unmanageable products of its reactions with alcoholates indicated that they were not the simple formation of alkyl ethers, which had been proved to take place with the other compounds. The results of our preliminary experiments with sodic alcoholates show the expected retarding action of the amino group and the accelerating effect of the iodine, which, however, seems to be less active than the nitro group.¹ In all our experiments sodic methylate entered into reaction much more sluggishly than sodic ethylate.

The one really definite result of our work in this line was the great inertness of all of these compounds, except the tribromdinitrobenzene, toward aniline, the amount of reaction being trifling after long heating at 100° or even at the boiling point of aniline.² This shows that the amino group, hydrogen, or iodine, exercises much less loosening effect on the bromine than a second nitro group in the same position, since tribromdinitrobenzene is converted into trianilinodinitrobenzene³ by short heating. A third nitro group (in 2,4,6-tribromo-1,3,5-trinitrobenzene) produces the complete replacement of the bromine in the cold, whereas the dinitro body does not react until heated.

EXPERIMENTAL

Preparation of 2,4,6-Tribrom-3-nitraniline according to Körner⁴

As Körner does not give very full directions for this process, we describe our work in detail. Ten grams of *m*-nitraniline were dissolved in a liter of strong hydrochloric acid and diluted up to 7 liters. A stream of air saturated with bromine vapor was then drawn through this solution, until an excess was indicated by the change of the color of the liquid from yellow to light red. The tribromnitraniline, which began to separate toward the end of the process, was washed with water, then with dilute ammoniac hydroxide, and finally again with water, after which it was purified by crystallization from alco-

¹ Compare THIS JOURNAL, 13, 164 (1891); 14, 363 (1891).

² *Ibid.*, 14, 363 (1891).

³ *Ibid.*, 11, 448 (1889).

⁴ Gazz. chim. ital., 1874, 348.

hol, until it showed the melting point $101^{\circ}.5$. Körner gives $102^{\circ}.5$, but we have never succeeded in raising it above the temperature given by us. Our thermometer was found to register 100° in steam.

0.2201 gram substance gave 0.3315 gram AgBr.

	Calculated for $C_6HBr_3NO_2NH_2$	Found
Br	63.97	64.07

Study of the Method of Remmers¹ for Preparing 2,4,6-Tribrom-3-nitraniline

Tribromacetanilide was made by boiling under a reverse condenser for 2 hours a mixture of tribromaniline, acetyl chloride and glacial acetic acid. The product crystallized in long, white needles and melted at 232° . Remmers gives the same melting point for this substance.

Ten grams of this tribromacetanilide dissolved in 50 cc. of fuming nitric acid (specific gravity 1.50) were heated on the steam bath until the first brown fumes appeared, which happened from 45 seconds to one minute after the heating began. The product was then diluted with water, when a sharp odor was noticed, probably the dibromdinitromethane observed by Bentley.² The precipitate was semisolid and yellow at first, but turned reddish brown on exposure to the air. After the mass had stood for 2 weeks it was crystallized at first from alcohol, and then from benzene, until it showed the constant melting point 208° – 209° . Remmers does not give the melting point of this substance.

Half a gram of the compound was heated under a return condenser for 5 hours with 30 cc. of sulphuric acid of specific gravity 1.44, when the solid turned from white to yellow, and after crystallization from alcohol showed the constant melting point $101^{\circ}.5$, and crystallized in star-shaped clusters of needles, so there can be no doubt that it is identical with the tribromnitraniline obtained according to Körner.

2,4,6-Tribrom-3-nitrodiaacetanilide, $C_6HBr_3NO_2N(C_2H_5O)_2$.—Fifteen grams of tribromnitraniline dissolved in 30 grams of

¹ Ber. d. chem. Ges., 7, 351 (1874).

² THIS JOURNAL, 20, 472 (1898).

glacial acetic acid were boiled under a return condenser for 2 hours with 30 grams of acetyl chloride and a little anhydrous sodic acetate. The white product was crystallized from alcohol until it showed the constant melting point 168° – 169° . It is evidently therefore the substance melting at 169° obtained by H. L. Wheeler¹ in the same way, and supposed by him to be the monacetanilide. Remmers,² who had prepared it previously, recognized it as the diacetanilide, but gave no melting point.

0.2110 gram substance gave 0.2604 gram AgBr.

	Calculated for $C_8HBr_3NO_2N(COCH_3)_2$	Found
Br	52.25	52.53

Properties of 2,4,6-Tribrom-3-nitrodiacetanilide.—White octahedra, or dodecahedra, which melt at 168° – 169° . It is soluble in acetone, slightly soluble in cold chloroform, benzene, or glacial acetic acid, more soluble in these liquids when hot; very slightly soluble in cold alcohol, or methyl alcohol, more soluble hot; almost insoluble in cold ligroin, slightly soluble in hot; essentially insoluble in water whether cold or hot. The best solvent for it is alcohol or acetone. Hot sodic hydroxide solution converts it into the monacetanilide.

2,4,6-Tribrom-3-nitracetanilide, $C_8HBr_3NO_2NHCOCH_3$.—This substance could be made by treating the tribrom-nitranilide with a little more than the calculated amount of acetyl chloride in glacial acetic acid, but we found it more convenient to prepare the diacetanilide as already described, and then remove one of the acetyl groups with sodic hydroxide. Ten grams of tribromnitrodiacetanilide were heated with a solution of sodic hydroxide (5 grams in 100 cc.), and, as the liquid became warm, the diacetanilide went into solution. After it had been boiled for 15 minutes, hydrochloric acid was added, which threw down a white precipitate, and this was purified by crystallization from alcohol until it showed the constant melting point 208° – 209° . This substance was made

¹ THIS JOURNAL, 17, 702.

² Ber. d. chem. Ges., 7, 351 (1874).

by Remmers¹ by the action of nitric acid on tribromacetanilide, but he gave no melting point.

0.1748 gram substance gave 0.2366 gram AgBr.

	Calculated for $C_6HBr_3NO_2NHC_2H_5O$	Found
Br	57.55	57.59

Properties of Tribromnitracetanilide.—It forms white, rhombic crystals from alcohol, methyl alcohol, or glacial acetic acid, needles from benzene. It melts at 208°–209°. It is soluble in cold glacial acetic acid, more so in hot; slightly soluble in cold alcohol, or acetone, more soluble in hot; practically insoluble in cold ether, slightly soluble in hot; essentially insoluble in water, or ligroin, hot or cold. It is distinctly less soluble than the diacetanilide. The best solvent for it is alcohol or acetone. Heating with sodic hydroxide for 15 minutes or more does not remove the acetyl group. The action of nitric acid upon it was studied under many different conditions. The principal product was bromanil, identified by its color and crystalline form.

The behavior of 2,4,6-tribrom-3-nitraniline was studied with various reagents, and, although no new substances were isolated, a brief account of our results seems to us worth while. Aniline, when warmed with the tribromnitraniline on the steam bath for 6 hours, had little or no effect, as the original substance was recovered unaltered. After 6 hours at the boiling point of aniline a blue-black substance, probably aniline black, was formed, but apparently in no great amount, as in this case also we succeeded in recovering the greater part of the original substance.

Sodic ethylate or methylate did not act on the tribromnitraniline at ordinary temperatures, since no test for bromide was obtained, after the compounds had stood together for 2 or even 5 months. When the mixture was heated, sodic ethylate produced no sodic bromide below 70°, and even at this temperature it was necessary to heat for 3 hours to obtain a faint test, which was hardly increased by 2 hours more, but, when the temperature was raised to 80°, a strong test was ob-

¹ Ber. d. chem. Ges., 7, 351 (1874).

tained in half an hour. Sodid methylate acted much more slowly, as heating it with the tribromnitraniline to 100° gave no action in half an hour, and a strong test for bromide was not obtained till after $2\frac{1}{4}$ hours. Even after 4 hours much unaltered substance was recovered, and the original compound did not begin to disappear till after 8 hours. 2,4,6-Tribrom-3-nitrobenzene gave a strong test for bromide after half an hour, when exposed to the same conditions.

As the tribromnitracetanilide is very stable toward sodic hydroxide, we tried the action of sodic alcoholates upon it in the hope that the acetyl group might diminish the retarding effect of the amino group enough to bring about a reaction with the bromine, before the amino compound was formed. With sodic methylate tests were made at measured intervals, and it was found that a faint indication of bromide appeared only after $2\frac{1}{4}$ hours on the steam bath, and that it did not become strong until the mixture had been heated more than $5\frac{3}{4}$ hours; as the tribromnitraniline gave a strong test in $2\frac{1}{4}$ hours, the acetanilide acted more slowly than the free amine. Sodid ethylate gave a strong test after 4 hours on the steam bath (it was not tested earlier), so its action here also is distinctly more vigorous than that of the methylate. No test for nitrite was obtained in any of these experiments. The organic products of these reactions were reddish brown and amorphous; they did not melt below 280° , and were but slightly soluble in all the organic solvents. We did not succeed in bringing them into a state fit for analysis.

1-Iod-2,4,6-tribrom-3-nitrobenzene, $C_6HIBr_3NO_2$.—Ten grams of tribromnitraniline were dissolved in 150 cc. of glacial acetic acid and mixed with 50 cc. of sulphuric acid diluted with an equal volume of water. The mixture was cooled with ice, and shaken for some time so that only small crystals of the aniline should form, since large ones would have resisted the diazotization. To the cold mixture 2.5 grams of sodic nitrite dissolved in 10 cc. of water were added in small portions at a time with thorough shaking, the addition taking half an hour. As the diazo reaction took place, the semisolid mass changed from yellow to white and in order to

be certain that it was complete, the mixture was allowed to stand in the cooling bath for 2 hours; at the end of this time an ice-cold solution of 12 grams of potassic iodide was added gradually with thorough shaking, which took half an hour, during which time the mixture turned from white to very dark gray. After it had stood overnight, it was heated on the steam bath for three-quarters of an hour to form the iod-tribromnitrobenzene, the reaction being accompanied by a change of color from gray to yellow. The liquid was then cooled with ice to separate out as much of the iod compound as possible, and the solid was freed from iodine by washing it successively with a concentrated solution of potassic iodide, a solution of sodic thiosulphate, and finally with water. The yellowish white residue was then crystallized from alcohol until it was perfectly white and showed the constant melting point 144° – 145° . The average yield of the crude product was 52 per cent. of the theoretical.

0.2089 gram substance gave 0.3439 gram AgBr + AgI.

	Calculated for $C_6HBr_3INO_2$	Found
$Br_3 + I$	75.53	75.61

Properties of 1-Iod-2,4,6-tribrom-3-nitrobenzene.—It crystallizes from alcohol in white, rectangular plates which melt at 144° – 145° . It is very soluble in chloroform; soluble in cold benzene, very soluble in hot; fairly soluble in cold, more soluble in hot ether; slightly soluble in cold alcohol, or glacial acetic acid, more soluble in hot; essentially insoluble in water or ligroin, whether cold or hot. Alcohol is the best solvent for it.

Action of Sodic Ethylate on 1-Iod-2,4,6-tribrom-3-nitrobenzene. Iodtribromnitrophenetole, $C_6HIBr_3OC_2H_5NO_2$.—Twenty grams of iodtribromnitrobenzene dissolved in 100 cc. of dry benzene were mixed with a solution of sodic ethylate made by treating 3.75 grams of sodium with 100 cc. of absolute alcohol. There were therefore 4 molecules of ethylate for each molecule of the substituted benzene. The mixture was allowed to stand at ordinary temperatures for 10 days,

when it was found that a precipitate had formed, which was soluble in water, and gave tests for bromide, iodide, and nitrite. The filtrate from this precipitate was allowed to evaporate spontaneously, and, by pouring off the mother liquor at sufficient intervals, was divided into three portions, the first of which was a yellow, crystalline solid, the second a reddish, and the third a red oil. The crystalline portion was washed thoroughly with water and then recrystallized from alcohol, when after 8 crystallizations it showed the constant melting point 121° .

I. 0.1951 gram substance gave 0.2639 gram AgBr + AgI.

II. 0.1558 gram substance gave 0.2103 gram AgBr + AgI.

	Calculated for $C_6HIBr_2OC_2H_5NO_2$	I	Found	II
2Br + I	63.63	63.56	63.42	

The specimens used in the analyses came from two different preparations. The determination of the constitution of the substance must be left for future experiment.

Properties of Iodidibromnitrophenetole.—It crystallizes from alcohol in long, white, rectangular prisms, which turn slightly brown on standing. Melting point, 121° . It is very soluble in ether, chloroform, or glacial acetic acid; tolerably soluble in cold methyl alcohol or ligroin, more soluble in hot ligroin; slightly soluble in cold alcohol, soluble in hot; essentially insoluble in water, hot or cold. Alcohol is the best solvent for it.

The appearance of iodide and nitrite, as well as bromide, among the products of the reaction shows that other organic compounds were present beside the phenetole. They were undoubtedly contained in the mother liquors and the two oily fractions, but as yet we have not had time to study these thoroughly. From the first oily portion we isolated a substance melting at 149° but in too small quantity to determine whether it was pure, or to make an analysis. We hope one of us will be able to continue this work.

When the iodtribromnitrobenzene was heated with sodic ethylate solution, tests for bromide, iodide and nitrite were

obtained after 15 minutes, but the product was an uninviting tar, from which we did not succeed in isolating any definite compound in the time at our disposal.

Sodic methylate was much less active; after it had stood with the iodtribromnitrobenzene for 10 days at ordinary temperatures, no precipitate had been formed, and although the solution gave a test for a bromide and an iodide and a very faint one for a nitrite, the organic material seemed to consist mostly of the unaltered substance; and the same results were obtained from a mixture heated on the steam bath for 15 minutes.

The 1-iod-2,4,6-tribrom-3-nitraniline is very inert toward aniline. Two grams of it were heated on the steam bath for 10 days with 10 cc. of freshly distilled aniline. At the end of this time only a faint test for bromide could be obtained, and although the organic product was brown, several crystallizations from alcohol showed that it was made up principally of the unaltered substance melting at 144° - 145° .

CAMBRIDGE, MASS.
October 14, 1912

REACTIONS OF OZONE WITH CERTAIN INORGANIC SALTS

BY YOSHITO YAMAUCHI

Several workers, among whom we may mention Schönbein, Williamson, Maquenne and Mailfert, have studied the oxidation of certain inorganic salts by ozone, but report, for the most part, only the final products of the reactions and not the way in which the ozone has acted to bring them into existence. The author has therefore, at the suggestion of Prof. M. Chikashige, sought to get more accurate information upon this point, and presents the following as a brief account of his investigation:

1. Method of Investigation

Estimation of the Ozone which is to be Used for Oxidation.—To determine the concentration of ozonized oxygen before consuming it, there has existed only one method, that of di-

rectly weighing a certain known volume of it and of comparing this weight with that of an equal amount of pure oxygen. Since this method is by no means convenient, the author contrived a new one, that of filling two large cylindrical glass tubes of known volumes with one and the same sample of ozone, so that he could use one for the purpose of estimation and the other for the oxidation.

Take two tubes, *A* and *B*, of nearly equal capacity, 35 cm. in length and about 5 cm. in diameter. They are provided with glass cocks, *a* and *a'*, at one end, and with double cocks, *b* and *c* and *b'* and *c'*, at the other. They are mounted in a somewhat slanting position and connected with a bent tube at the lower end. Fig. I represents the arrangement. Keep-

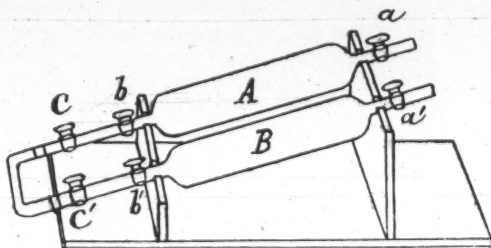
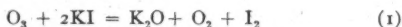


Fig. I.

ing now all the cocks open, ozonized oxygen is passed first from *A* to *B*, then from *B* to *A*, the amount of the gas passed each time being almost 1.5 times more than the total volume of the two tubes. Working regularly in this manner, it was always found that the amount of ozone in both tubes stood almost in a constant ratio, as will be seen below.

Comparison of the Amount of Ozone in the Two Tubes.—After having filled the tubes with ozonized oxygen, close all the cocks except *c* and *c'* and disconnect the tubes. Take then 2 aliquot portions of a neutral potassium iodide solution and pour them each into two different beakers, from which transfer them separately into the spaces between *b* and *c*, and *b'* and *c'*, respectively. Then, shutting off the cocks *c* and *c'* and open-

ing the others, b and b' , let the solutions into the cylindrical parts of the tubes, and shake vigorously until they no longer give the odor of ozone. The solutions now containing liberated iodine are thoroughly washed down into their original vessels, and, after being acidified with a few drops of dilute sulphuric acid, are titrated for iodine by means of a standard solution of sodium thiosulphate.¹ The amounts of the ozone corresponding to these quantities are calculated from the well established equation:



The amount of ozone thus found in the two tubes is compared after being recalculated on the basis of a liter volume and the mean ratio taken from six such determinations, as will be seen from the following table:

Table I

No.	Ozone in gram		Ozone in gram		a/b
	Per 671 cc. (Tube A)	Per liter (a)	Per 693 cc. (Tube B)	Per liter (b)	
1	0.0058	0.0087	0.0062	0.0089	0.98
2	0.0053	0.0080	0.0058	0.0083	0.96
3	0.0048	0.0071	0.0044	0.0064	1.11
4	0.0081	0.0120	0.0087	0.0126	0.95
5	0.0032	0.0048	0.0032	0.0046	1.04
6	0.0147	0.0219	0.0151	0.0217	1.01

Mean, 1.01

Now, by the aid of this, we can easily calculate the amount of ozone in one tube, upon actually finding that in the other.

Manner of Ozone Decomposition during the Process of Oxidation.—Taking a known amount of ozone, the author caused it to act upon a salt in solution, whose amount was known and was greater than one equivalent as compared with the ozone used. When the reaction was over, he estimated the amount of the oxidized salt, from which, by taking account of the amount of ozone used, he could directly infer how the ozone decomposed before the oxidation; whether as



¹ Cf. Treadwell and Anneler: *Z. anorg. Chem.*, **48**, 87 (1906).

where only one-third the oxygen atoms would have entered into the reactions, or as



where all three atoms would have taken part in the oxidation. With the aid of such inferences, he established chemical equations to represent the oxidizing action of ozone according to the various cases.

II. Reactions of Ozone Investigated according to this Method

1. *Arsenious Acid*.—That metallic arsenic is oxidized by ozone finally to arsenic acid was first made known by Schönbein.¹ The determination of ozone by the use of arsenious acid² is based on this reaction.

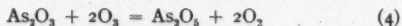
The author took a known amount of ozone contained in a cylindrical tube, let in an aliquot portion of a neutral potassium arsenite solution, and allowed the mixture to react for about half an hour, the quantity of the oxidized salt being then calculated from the amount of the unchanged arsenite, as determined by the use of a standard iodine solution. The ratio of the ozone to the arsenite oxidized is given in the following table:

Table II

No.	Ozone in gram	Arsenious acid oxidized by the ozone in gram	Arsenious acid per gram ozone in grams
1	0.0093	0.0204	2.19
2	0.0080	0.0149	1.86
3	0.0059	0.0138	2.34
4	0.0116	0.0243	2.10
5	0.0098	0.0215	2.19

Mean, 1 : 2.14

This reaction is, therefore, well represented by the usual equation:

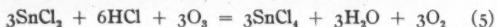


as it requires 2.06 grams arsenious oxide per gram ozone.

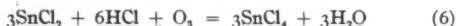
¹ Ann. Chem. (Liebig), **89**, 288 (1854).

² Thénard: Compt. rend., **76**, 174; Hartley, J. Chem. Soc., **39**, 120 (1881). Treadwell and Anneler: Z. anorg. Chem., **48**, 94 (1906).

2. *Stannous Chloride*.—The conversion of a stannous into a stannic salt by ozone has been studied by Schönbein¹ and Williamson.² If the reaction is, as in other cases,



the amount of the stannous chloride oxidized by ozone would be in the ratio of 3.96 grams to 1 gram of the latter. But, if the reaction takes place as follows:



the ratio would be 11.87 grams stannous chloride to 1 gram ozone; besides, the pressure in the reaction tube would be then very much reduced, since oxygen is no longer produced in a volume equal to the ozone consumed.

According to the author's experiments, the reaction seems to proceed exactly as shown in Equation (6), and not as in (5). After a known quantity of a stannous chloride solution in hydrochloric acid had been mixed in the usual manner with a known quantity of ozone, and left for about half an hour with constant shaking, the amount of the stannous chloride entering into reaction was calculated from the amount of the unoxidized salt, which was found by the use of a standard iodine solution, subtracted from the total amount of the salt taken. The results of the experiments are given in the following table:

Table III

No.	Ozone in gram	Stannous chloride oxidized by the ozone in gram	Stannous chloride per gram ozone in grams
1	0.0077	0.1147	14.89
2	0.0119	0.1550	13.03
3	0.0089	0.1392	15.64

Mean, 1 : 14.52

This ratio nearly coincides with that calculated from Equation (6). That it is a little more than the latter is due, perhaps, to the simultaneous action of the co-existing ordinary oxygen. It must, however, not be forgotten that what causes the re-

¹ Ann. Chem. (Liebig), 89, 293 (1854).

² *Ibid.*, 81, 14 (1847).

action for the main part is the ozone and not the oxygen, because the reaction goes on very rapidly only at first, and as soon as the ozone is used up, the reaction becomes notably slower. Thus, the two tubes, *A* and *B*, were equally filled with ozone, and treated with equal quantities of a stannous chloride solution. One of the tubes was then left for only 20 minutes, and the other for a much longer interval of time. The oxidation stopped after a certain lapse of time; the degrees of oxidation in both tubes, expressed in terms of the stannous chloride, were nearly the same in spite of so great a difference in time. The results of four such experiments are given in Table IV.

Hence, we have here a new instance of oxidation by ozone, in which the latter acts by decomposing itself according to Equation (3).

Table IV

Time in minutes	Degrees of oxidation in terms of stannous chloride	<i>r</i> / <i>i</i>
20	0.1368	1/1.07
140	0.1468	
20	0.2015	1/1.05
100	0.2120	
20	0.1795	1/1.15
60	0.2062	
20	0.2255	1/0.95
40	0.2133	

Mean, $1 : 1.06$

3. *Sodium Thiosulphate*.—The action of ozone on sodium thiosulphate seems not to have been studied hitherto by any chemist. When a solution of this salt is shaken with ozone, it becomes milky through the separation of sulphur, while the solution, which remains quite neutral during the reaction, contains sulphite and sulphate, besides some unchanged thiosulphate.

Whether or not a part of the sulphite and sulphate comes from the oxidation of the precipitated sulphur by ozone cannot yet be definitely decided, because sulphur is oxidizable, according to Mailfert,¹ while according to Schönbein² it is not.

¹ Compt. rend., 94, 1186 (1882).

² Ann. Chem. (Liebig), 89, 282 (1854).

With regard to the author's experiment, in which he passed ozone a long time through the precipitated sulphur, with neutral reaction, suspended in water, he could find only an almost insignificant quantity of sulphite formed. However, in order to make the problem as simple as possible, he did not take into account the presence of sulphite from such a source.

Then, the quantitative estimation of the reactions was effected in the following manner:

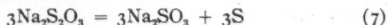
As usual, a known amount of a sodium thiosulphate solution was introduced into the tube containing a known amount of ozone, and the mixture was allowed to stand for about half an hour with frequent shaking. After being separated from the precipitated sulphur, the solution was then examined for its iodine equivalent (6, V) (the latter covers the amount of both the thiosulphate in excess and sulphite). Barium chloride was added to this solution, precipitating all the sulphates, a part of which had been originally present through the oxidation of the thiosulphate by ozone, and the rest derived from the sulphite oxidized by iodine. The amount of the sulphates (1, V) therefore corresponded to the total weight of the thiosulphate entering into reaction (2, V) with a definite volume of ozone: cf. Equation (9). Then, from the excess (4, V) of the thiosulphate originally taken (3, V) over that actually entering into reaction (2, V), may be directly calculated its iodine equivalent (5 V), and the difference (7, V) between this value and that determined before (6, V), which is a little greater, gives exactly the amount of the sulphite, the amount of the thiosulphate corresponding to it being then calculated from it (8, V). The amount of the thiosulphate changing into the sulphate (9, V) can be also calculated by taking the difference of the above quantity from the total amount of the thiosulphate entering into the reaction (2, V). The ratio of the thiosulphate changing either into the sulphite or into the sulphate becomes nearly 1:2 from the mean of four such experiments, as will be seen from the following table:

Table V

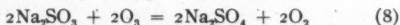
No.	Description	I	II	III	IV
1	Barium sulphate (found)	0.0733	0.1244	0.0826	0.1024
2	Sodium thiosulphate entering into reaction (calc. from 1)	0.0496	0.0843	0.0560	0.0694
3	Sodium thiosulphate originally taken (found)	0.1606	0.1606	0.1606	0.1606
4	Excess of sodium thiosulphate escaping the reaction (diff. between 3 and 2)	0.1110	0.0763	0.1046	0.0912
5	Iodine equivalent to the above salt (calc.)	0.0891	0.0613	0.0840	0.0732
6	Iodine equivalent to the thiosulphate solution soon after the reaction with ozone (found)	0.1146	0.1142	0.1144	0.1148
7	Difference between 5 and 6	0.0255	0.0529	0.0304	0.0416
8	Sodium thiosulphate changing into the sulphite ¹ (calc. from 7)	0.0159	0.0329	0.0190	0.0259
9	Sodium thiosulphate changing into the sulphate (diff. between 2 and 8)	0.0337	0.0514	0.0370	0.0435
10	Ratio of 8 to 9	1 : 2.1	1 : 1.6	1 : 2.0	1 : 1.7
			Mean, 1 : 2		

¹ From the equation, $2\text{I} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} = 2\text{HI} + \text{Na}_2\text{SO}_4$, we see that two atoms of iodine are equivalent to 1 molecule of sodium sulphite, which is now in its turn equivalent to one molecule of sodium thiosulphate.

Hence we find that 2 molecules of sodium sulphate are always produced together with 1 molecule sodium sulphite. Perhaps we have no other way of understanding this reaction than by supposing it to take place in two successive stages. The first is the catalytic decomposition of the thio-sulphate into sulphite and sulphur, where the ozone effects no oxidation at all; thus



Then follows the second stage, in which only two out of the three molecules of sodium sulphite are acted upon by ozone, so that the reaction may be expressed as follows:



Since we know the amount of ozone necessary to effect the oxidation of thiosulphate, as shown in (9, V), into sulphate, we can calculate the amount of the oxidized thiosulphate per gram ozone, thus:

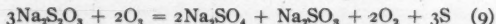
Table VI

No.	Ozone in gram	Sodium thiosulphate changed into the sulphate in gram	Sodium thiosul- phate per gram ozone in grams
1	0.0101	0.0337	3.34
2	0.0173	0.0514	2.97
3	0.0111	0.0370	3.33
4	0.0139	0.0435	3.13

Mean, 1 : 3.19

Calculated for 1 molecule sodium thiosulphate per molecules ozone, as may be deduced from equation (8), we have the ratio 1 : 3.29, which is really in good accord with the experimental ratio.

Combining now the 2 equations (7) and (8), we establish the following to account approximately for the whole course of the reaction of ozone with sodium thiosulphate:



4. *Thallous Nitrate*.—Schönbein¹ first studied the oxidation of thallium or thallous hydroxide by ozone in the presence of water. Schöne² applied this reaction to the quantitative

¹ J. prakt. Chem., **93**, 36 (1864); *Ibid.*, **95**, 470 (1865).

² Ber. d. chem. Ges., **13**, 1508 (1880).

analysis of ozone, making use of test paper soaked in thalious hydroxide solution, where the depth of the color of the thallic oxide formed should vary according to the amount of ozone present. Lamy¹ settled the composition of thallic oxide, dried at 100°, to be $Tl_2O_3 \cdot H_2O$, while Rabe² claims to have obtained the anhydrous oxide, Tl_2O_3 , by oxidizing an alkaline solution of a thalious salt with hydrogen peroxide.

According to the author's experiments, the water in the thallic oxide seems never to be equal to one molecule, as was shown by Lamy. So, it may be urged that hydrated thallic oxide is very liable to lose its water in part even when dried below 100°. He also determined as usual the amount of thallic oxide precipitated equivalent to the ozone used, from the results of which the equation for the reactions could be well established.

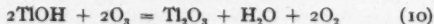
An ammoniacal solution of thalious nitrate was taken for the purpose of experiment. An aliquot portion, after being introduced into the tube containing ozone, was shaken vigorously for a few minutes only. The voluminous brown precipitate was then washed, collected on a weighed filter, dried in an air bath below 100°, and finally weighed. The results of the experiments are given in the following table:

Table VII

No.	Ozone in gram	Thallic oxide precipitated by the action of ozone in gram	Thallic oxide per gram ozone in grams
1	0.0206	0.1038	5.04
2	0.0151	0.0618	4.09
3	0.0201	0.0952	4.74
4	0.0147	0.0750	5.10
5	0.0139	0.0716	5.15
6	0.0182	0.0857	4.71
7	0.0139	0.0635	4.57

Mean, 1 : 4.77

If the reaction be represented as follows:



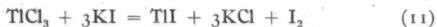
and the oxide be considered to retain no water at all, then the

¹ Ann. chim. phys., [3] 67, 385.

² Z. anorg. Chem., 48, 428 (1906).

ratio of ozone to the oxide formed is 1 : 4.76, in good accord with the experimental data.

Now, in the hope that the composition of thallic oxide might be better established, the author converted 0.5096 gram of well dried oxide into thallic chloride, added a certain quantity of potassium iodide, and then determined the amount of iodine liberated from it. The amount of thallium equivalent to iodine was calculated from the equation,



and then recalculated to thallic oxide, Tl_2O_3 , with no water, as 0.4970 gram. The loss of weight from the original 0.5096 gram, about 2.4 per cent., may be due to some quantity of water still retained.

That the oxidation of a thallic salt by ozone goes on rapidly and completely, and that the thallic oxide thus formed can be very easily weighed, affords surely another very convenient method for the gravimetric determination of ozone, in contrast to that of Schöne.¹ It is then only necessary to take proper care to dry the oxide always at a constant temperature, in order to have the water regularly expelled.

5. *Mercurous Nitrate*.—According to Mailfert,² mercurous salts in solution are easily oxidized by ozone partly to mercuric salts, which go into solution, and partly to basic salts, which remain undissolved.

The author examined the action of ozone on mercurous nitrate in the presence of an excess of nitric acid, and found that the oxidation takes place, though very slowly and incompletely, there remaining always some odor of ozone. The formation of basic salts was not perceived, because there was present much excess of nitric acid.

The amount of the mercuric salt formed was determined from the quantity of the unchanged mercurous salt remaining, which was precipitated and weighed in the form of chloride. The results of the experiments are as follows:

¹ *Loc. cit.*

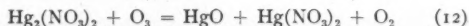
² *Compt. rend.*, 94, 860 (1882).

Table VIII

No.	Ozone in gram	Mercurous nitrate oxidized by ozone in gram	Mercurous nitrate per gram ozone in grams
1	0.0100	0.0919	9.19
2	0.0066	0.0614	9.30
3	0.0108	0.1090	10.09
4	0.0110	0.1101	10.01
5	0.0090	0.0807	9.63

Mean, 1 : 9.64

Calculated for the equation,



the ratio of ozone to mercurous nitrate is 1 : 10.94, wherein the difference from the experimental data shows the incompleteness of the reaction.

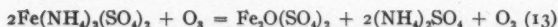
6. *Ferrous Ammonium Sulphate*.¹—A solution of this salt was treated in the usual manner with ozone, and the amount of oxidized salt was determined by subtracting the unchanged ferrous salt, as determined with potassium permanganate, from the total quantity of ferrous salt originally taken. The ratio of the ozone to the oxidized salt was found from the following data:

Table IX

No.	Ozone in gram	Ferrous ammonium sulphate oxidized by ozone in gram	Ferrous ammonium sulphate per gram ozone in grams
1	0.0023	0.0332	14.43
2	0.0111	0.1484	13.37
3	0.0047	0.0666	14.17
4	0.0064	0.0809	12.64

Mean, 1 : 13.65

Calculated for the equation,



the ratio is 1 : 11.83. The difference between the experimental ratio and the theoretical must be due to the simultaneous action of ordinary oxygen, as we have seen in the case of stannous chloride.

¹ Schönbein, *Ann. Chem. (Liebig)*, **89**, 293 (1854), makes the statement that the ferrous salt is oxidized by ozone to the ferric state.

7. *Tellurous Oxide*.¹—By passing ozone into tellurous oxide suspended in water, no appreciable amount of oxidation products could be detected.

8. *Titanium Dioxide*.—Since titanium dioxide dissolved in concentrated sulphuric acid is very easily oxidized by hydrogen peroxide, the author made certain tests as to whether it is also oxidized by ozone. The results, however, were always negative.

9. *Chloropalladous Acid*.—According to L. Wöhler and King,² oxidation of this compound by ozone takes place in the following manner:



But, as there was found no convenient way of distinction between the palladic and palladious compounds, the author could not apply his method to test the correctness of the above equation.

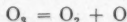
SUMMARY

1. As the concentration of ozone differs with every preparation, all methods of determining the concentration through the consumption of the gas must involve using up the preparation, i. e., when the concentration is known, the preparation no longer exists. The method of its determination by direct weighing is also not convenient. The author has, therefore, contrived a new method of dividing one sample into two parts, and of determining the concentration of the one by measuring that of the other by analysis.

2. So far as the author could determine, ozone seems to be decomposed according to the equation



only in the case of the oxidation of stannous chloride. The decomposition goes on, however, usually as follows:



3. The action of ozone on sodium^{as} thiosulphate has been studied by the author perhaps for the first time. There take

¹ Cf. Mailfert: *Compt. rend.*, **94**, 1186 (1882).

² *Z. anorg. Chem.*, **40**, 327 (1905).

place two reactions, in which the ozone seems first to cause the catalytic decomposition of the thiosulphate and then to be able to effect a partial oxidation of the sulphite formed.

4. Formation of thallic oxide from a thalious salt by ozone occurs very rapidly and completely. It may surely be utilized as a gravimetric method in the quantitative determination of ozone.

KYOTO, Sept. 20, 1912

[Contributions from the Sheffield Laboratory of Yale University]

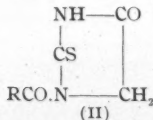
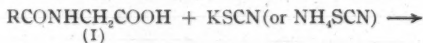
HYDANTOINS

THE ACTION OF THIOCYANATES ON α -AMINO ACIDS

[TWENTIETH PAPER]

BY TREAT B. JOHNSON

The writer desires to call attention, in this note, to an error which unfortunately occurs in some of the recent publications from this laboratory on thiohydantoins. It has been shown that an acyl derivative of an α -amino acid (I) (hippuric acid, etc.) enters into an important reaction with a thiocyanate in the presence of acetic anhydride and acetic acid. They combine, forming the corresponding acylthiohydantoins (II) as represented by the equation below. Of the several α -amino acids so far examined, glutaminic and aspartic acids are the only ones which have failed to react in this manner.



During the progress of our investigation of this interesting class of sulphur compounds my coworkers generally reported excellent yields by application of this reaction, but sometimes, however, the results obtained were very unsatisfactory. At first, no explanation could be offered for these failures, but it finally developed, after many experiments by the writer, that

the results were always unsatisfactory when we used potassium thiocyanate from a certain bottle, which had been in stock for fully six years. On the other hand, the other specimens of potassium thiocyanate, which were imported from Kahlbaum specially for our investigation, gave excellent results.

I now find that all of our thiocyanate (6 kilograms), with the exception of the bottle which failed to give the results desired, is mislabeled and is pure ammonium thiocyanate instead of potassium thiocyanate as represented by the Kahlbaum label. Consequently the yields given in the following publications: *Journal of the American Chemical Society*, 33, 1974; *Journal of Biological Chemistry*, 11, 97; *THIS JOURNAL*, 47, 242; 48, 103, were obtained by using ammonium thiocyanate instead of the potassium salt.

The most striking difference in behavior is observed when applying our reaction to hippuric acid. The product of the reaction is the same with both salts, but with potassium thiocyanate the product is oily and solidifies only after long standing, while, on the other hand, the ammonium salt reacts smoothly under similar conditions, giving a hydantoin which solidifies immediately on pouring into water.¹ Because of the remarkable difference in behavior of these two thiocyanates towards hippuric acid, we are now making a comparative study of their action on other α -amino acids.

The writer has always had the greatest confidence in the purity of Kahlbaum's preparations, but from his experience in this case and others it is evident that it will be necessary, hereafter, to test their reagents and not trust to their label.

NEW HAVEN, CONN.
Nov. 11, 1912

OBITUARY

JOHN WILLIAM MALLET

After a brief illness, Dr. Mallet closed his useful and honored life on Nov. 6, 1912, at the University of Virginia where he

¹ Mr. Marston L. Hamlin, of the Harriman Research Laboratory, New York City, writes me that he also obtained unsatisfactory results when he attempted to prepare benzoylthiohydantoin from hippuric acid and potassium thiocyanate. It is a pleasure to record my appreciation of the spirit that has characterized his correspondence.

had served as professor for forty years. Dr. Mallet was born of English parents near Dublin, Oct. 10, 1832. His father, Robert Mallet, was a civil engineer and a Fellow of the Royal Society. While at a classical school in Dublin, he developed interest in physics and chemistry through reading in his father's library the works of Black, Lavoisier, Fourcroy, Davy, Thomson, etc.

In 1848, he began analytical chemistry under Dr. James Apjohn, lecturer on chemistry at the Royal College of Surgeons in Dublin, and received private practical instruction in his laboratory. In 1849 he entered Trinity College, University of Dublin, and in that year published in the *Journal of the Geological Society of Dublin* a paper entitled "A Chemical Examination of Killinite." During the following three years he assisted his father in experiments upon the velocity of transmission of shocks from gunpowder explosions through rock and through loose earth, and also in the preparation for the British Association of an earthquake catalogue of 597 pages, extending from 1606 B.C. to 1842 A.D., all of which matter was collected and collated through a large amount of reading in different public libraries by the son before he was twenty-one years of age.

In 1851 he studied and worked under Professor Wöhler and formed a friendship with him which was kept up through life by numerous kindly letters. In 1852 he received the degree of Ph.D. at Göttingen, his thesis being a report upon the chemical examination of Celtic antiquities in the Museum in Dublin. During two vacations, he, with his fellow student, Wm. S. Clark, of Massachusetts, traveled through many manufacturing cities and mining districts of central Europe, so obtaining much information upon chemical manufactures at first hand.

In 1853 he came to the United States, primarily to collect certain engineering information for his father. Here he joined his friend, Dr. Clark, then professor of chemistry at Amherst, Mass., and shortly Dr. Mallet was elected professor of analytical chemistry in that college, where he remained but one session. The next year he was appointed chemist to the Geological Survey of Alabama, and professor of chemistry at the University of Alabama, and here he remained until 1861.

It was during these years he published in the *American Journal of Science* the analyses of a number of rarer minerals, mostly from American localities—beryl, tin pyrites, idocrase, schrotterite, etc.,—numerous analyses made for the Geological Survey and in 1856 a re-determination of the atomic weight

of lithium, also in 1857 a report upon the atomic weight of aluminum.

In May, 1862, Dr. Mallet, then, as always, a British subject, was given general supervision of the manufacture of ammunition for the Southern Confederacy, in which capacity he was most actively engaged throughout the war. This work was pushed on with such indomitable courage, patience, wisdom and skill that at the time of the surrender there was a large supply of ammunition on hand, stored near Macon, Ga.

In 1865, following peace, Colonel Mallet soon was employed by some northern capitalists to search for petroleum in Louisiana and eastern Texas. In the fall of that year he entered upon the duties of professor of chemistry in the medical department of the University of Louisiana, at New Orleans (since, Tulane University), and then organized a practical laboratory course in chemistry for medical students. During the three years passed here he devoted much time to the study of medicine and before leaving received the degree of Doctor of Medicine. This cultivation of an interest in the chemical side of medicine resulted in after years in a number of investigations in this line.

In the spring of 1868, Dr. Mallet came to the University of Virginia to organize and build up the School of Analytical and Industrial Chemistry, and in this he conducted what is thought to be the first systematic course in industrial chemistry in the United States. As an adjunct in teaching the latter course, he accomplished the collection of an extensive and comprehensive museum of chemical manufactures probably not surpassed in this country.

Here he built up the school from which came many of the teachers of chemistry in the colleges of the southern states and numbers of industrial chemists. In 1872 he was made professor of general and industrial chemistry, which work he conducted until in 1883 he accepted a professorship in the University of Texas. The next year he received a similar appointment at the Jefferson Medical School in Philadelphia and in the following session returned to his work at the University of Virginia, and remained there until his death.

As a lecturer he was most systematic, concise and deliberate, sparing no pains to present every thought and illustration with decisive clearness. His lectures made an indelible impression upon the teachable students.

Long is the roll of those who will ever recall with thankfulness the privilege of sitting under his teaching, realizing they were obtaining some insight into the wonders of nature from a master

mind and master worker; many, too, there receiving an inspiration which in after years led to vigorous research and confident initiative in the pursuit of their profession.

Dr. Mallet published in all over 100 papers upon unfamiliar chemical compounds, peculiar minerals, chemical and physical phenomena, meteoric stones and irons, volcanic dust and a number relating to the chemistry of medicine.

In 1877 he was elected a Fellow of the Royal Society and in 1880 presented to this society a revision of the atomic weight of aluminum and in 1889 a revision of the atomic weight of gold.

As an analytical and consulting chemist, his services were often sought in the examination of water, ores and manufactured products. Upon many occasions he was called to serve as expert witness in medico-legal cases.

In 1880, he was employed by the U. S. National Board of Health to conduct an investigation of the chemical methods in use for the determination of organic matter in potable waters. This considerable undertaking required more than two years and in it he had the services of four assisting analysts, conducting the work in the laboratory of the Johns Hopkins University, in Baltimore, in the laboratory of the Surgeon General at Washington and at the University of Virginia.

In 1877 he delivered a course of (20) lectures at the Johns Hopkins University on the "Utilization of Waste Materials," and in 1878 a similar course on the "Early History of Chemical Industries."

Among many appointments of honor and trust he was, upon three occasions, on the Assay Commission of the U. S.; a Judge of Awards at the International Exposition of 1876 at Philadelphia; and a member of the American Committee for the International Congress of Applied Chemistry for 1903 at Berlin and for 1906 at Rome. He was one of the founders of the American Chemical Society and a fellow or member of many other scientific societies of national repute.

He was given the degree of LL.D. by the William and Mary College, Va., and by the University of Mississippi (1872); Princeton University (1896); Johns Hopkins University (1902); and University of Pennsylvania (1906).

Dr. Mallet never strove for place or power, but, in all positions and under all circumstances, quietly and simply did his duty to the best of his very superior ability, with absolute integrity and no thought of self, but kind consideration for others. He was a devout Christian, a member of the Protestant Episcopal Church, very reserved, but very direct in expression of his Faith, when there was any occasion for it.

After teaching for fifty years, Dr. Mallet accepted the offer of a retiring allowance from the Carnegie Fund, ceasing to teach, but he continued active in his professional work up to the Eighth International Congress of Applied Chemistry in which he took part shortly before his last sickness.

Dr. Mallet was married twice. His first wife was Mary E., daughter of Judge Ormond, of Alabama, his second, Mrs. Josephine (Pages) Burthe, of New Orleans. He had three children by his first wife: John O., who died Feb., 1884, in Texas, Robert W. Mallet, Attorney at Law, of Norfolk, and Mrs. Mary C. Elliott, of Savannah, Ga.

F. P. DUNNINGTON

REVIEWS

TRATTATO DI CHIMICA ORGANICA GENERALE E APPLICATA ALL'INDUSTRIA, DOTT. ETTORE MOLINARI, Professore di Chimica industriale alla Società d'Incoraggiamento d'Arti e Mestieri e di Merceologia all'Università Commerciale Luigi Bocconi in Milano. Seconda edizione riveduta e ampliata con 506 incisioni. Milano: Ulrico Hoepli. 1912. pp. xxiii + 1087. Price, L. 18.00.

The appearance of the first edition of this unique book has already been noted.¹ That a new edition is called for after only two years and that the book is being translated into English and German is evidence of the fact that it meets a real want. In no other work, to the reviewer's knowledge, can the reader so conveniently find information on the theory and practice of technical processes based on the properties and reactions of organic substances. In the present edition, while the material has not been increased in volume, many of the chapters have been completed, some amplified and a few new ones added. The greatest additions have been made in the chapters on coal tar, dyes, alkaloids, etc. The statistics of production, exports and imports have been extended to the end of 1910 and in some cases 1911.

C. A. R.

PER-ACIDS AND THEIR SALTS. By T. SLATER PRICE, D.Sc., Ph.D., F.I.C. of the Municipal Technical School Birmingham. Monographs on Inorganic and Physical Chemistry. Edited by ALEXANDER FINDLAY, D.Sc. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. vi + 123. Price, \$1.00.

In this volume of 120 pages, the author has brought together

¹ THIS JOURNAL, 44, 202.

all that is known on the subject of per-acids. The book is well written and very clearly expressed and contains references to all the investigations of any importance that have been carried out on this subject. It is a valuable reference book for anyone who wishes information on this subject.

J. E. G.

PRACTICAL CHEMISTRY FOR ENGINEERING STUDENTS. By ARTHUR J. HALE, B.Sc. (London), Lecturer and Demonstrator in Chemistry at the City and Guilds Technical College, Finsbury. With an Introductory Note by PROFESSOR R. MELDOLA, D.Sc., LL.D., F.R.S. London, New York, Bombay and Calcutta. Longmans, Green & Co. 1912. pp. xix + 192. Price, \$1.00.

The author has selected such material as he thinks will be of the greatest value to an engineering student and such as can be given in the limited time at his disposal. This includes experiments on the nonmetals and a few on metallic compounds, such as pigments, paints, etc.; a brief course in qualitative analysis and in volumetric and gravimetric quantitative analysis. The author has undertaken a difficult problem and one in which the personal equation of the student and the instructor plays an important role. This book could be used with certain students with success, while others would only acquire a limited manual dexterity but no understanding of the principles involved.

J. E. G.

DIE ELEKTROLYTISCHE ALKALICHLORIDZERLEGUNG MIT STARREN METALLKATHODEN. Von DR. JEAN BILLITER, Privatdozent an der Universität Wien. I. Teil. Mit 189 Abbildungen im Text. Monographien über angewandte Elektrochemie. XLI. Band. Halle a/S.:Verlag von Wilhelm Knapp. 1912. pp. x + 284. Price, M. 16.50.

The subject is to be treated in two volumes. The present volume is a compilation of the patents granted in Germany, Great Britain and the United States. The patents of each of the three nations are recorded in the chronological order of their issue; the German patents are subdivided into process and apparatus, diaphragm, construction of electrode, and material of electrode; English patents have a fifth division, electric connection; with the patents granted in the United States the divisions are omitted. Under the heading of process

and apparatus are given the claims and description, the present status in the arts, and a discussion of leading features. The introduction treats in a general way of the principles that govern the electrolytic decomposition of alkali chlorides; there are two indices, one contains the patent numbers in numerical order with the names of the patentees for Germany, England and the United States, the other the names of the patentees.

The book is a record of an immense amount of tedious but useful work patiently carried through. It is to serve as a foundation for Vol. II, which is to be devoted to a detailed description of industrial plants, and will be issued shortly.

H. O. HOFMAN

HANDBUCH DER PRESSEHEFENFABRIKATION. VON DR. PHIL. WILHELM KIBY, Gärungs-Chemiker und Techniker. Mit 255 Abbildungen im Text und auf 7 Tafeln. Neues Handbuch der chemischen Technologie (Bolley's chemische Technologie, dritte Folge), herausgegeben von DR. C. ENGLER, wirkl. geh. Rat und Professor an der Technischen Hochschule in Karlsruhe. Braunschweig: Druck und Verlag von Friedr. Vieweg & Sohn. 1912. s. xiv + 669. Preis, geh. M. 24; geb., M. 25.50.

The present work fills a gap in scientific and technical literature which for many years has been felt by those desirous of acquainting themselves in detail with the technique of compressed yeast manufacture. No work treating this subject comprehensively has been published since 1888, the literature being limited to a small number of articles appearing at irregular intervals in one or other of the technical or trade papers.

For this reason we feel that the appearance of this work is very timely and is, therefore, to be looked upon with great favor.

The author, who has spent the greater part of his life serving this industry, treats the subject from the standpoint of the practical man. He has not merely compiled a large amount of material and incorporated the same in book form, but rather has made a most careful selection and has constantly drawn upon his experience, acquired through long years of practice, in commenting upon the relative merits and demerits of the various processes. In fact, it is this very attitude of the author

which renders the book so valuable to both student and practitioner, for he unreservedly gives to the reader the benefits of his years of practice.

Although concerned largely with the practical side of compressed yeast manufacture, the author has realized the importance, even to the experienced man, of an understanding of the theory of the processes involved, in order to enable him to more fully comprehend their value and apply his practical knowledge to greater advantage. For this reason the author has also treated the theory of compressed yeast manufacture at some length.

The various chapters of the book treat: A. Of the historical development of compressed yeast manufacture. B. The raw materials employed. C. The important constituents of the raw materials for manufacture, viz., malting, mashing, etc., and the analytical control of these operations. E. Fermentation: 1. Historical; 2. Causes; 3. Products, etc. F. Compressed yeast manufacture: 1. The old process; 2. The new aeration process.

At the end of the book are appended, in the form of a folder, 7 diagrams of compressed yeast plants working according to the old and the new methods. A survey of all German patents pertaining to compressed yeast manufacture granted since 1877 is incorporated in this valuable work, and this feature will be especially welcomed by all who wish to acquaint themselves with the various improvements in mechanical appliances and processes.

Twelve tables for simplifying the calculation of analytical results are embodied in the work, and a carefully prepared bibliography including standard works and periodical publications, German, French and English, renders the work suitable for purposes of reference.

We must express regret, however, that the author does not seem to possess any knowledge of American conditions and the researches carried on in this country in many of the fields which are closely related to compressed yeast manufacture. Otherwise the subject matter is all carefully and comprehensively treated and the numerous excellent illustrations materially

increase its value. The paper and the type are both good, and the book as a whole conforms to the high standard set by all Vieweg publications.

R. WAHL

RESEARCHES ON CELLULOSE. III. (1905-1910.) By C. F. CROSS AND E. J. BEVAN. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1912. pp. x + 173. Price, \$2.50.

In this volume, which was delayed in order to include research work published in 1911, the authors have departed somewhat from the plan of the preceding volumes, I and II. Instead of recording in a general way the progress of industries employing cellulose as a basic material they have confined themselves to reviewing and commenting on about eighteen of what they consider to be the more important articles published during the period covered. The discussion of the subject, while showing a very deep knowledge of cellulose, is one which brings out theoretical and purely scientific information much more strongly than it does practical technical applications.

The book is divided into five chapters which cover the following subjects:

1. A general discussion of the relation of cellulose to biological science.
2. Normal cellulose and research throwing light on its constitution.
3. Cellulose esters.
4. Ligno-celluloses: their reactions and constants.
5. Technical developments. Of the 46 pages in this chapter, 24 are taken up by a discussion of the "Heart damage" of Jute, while other subjects briefly mentioned are constituents of raw cotton, textile bleaching processes, sizing paper with rosin compounds, cellulose acetate as wire insulation, etc.

The style in which this book is written renders its reading a difficult and laborious task, and it is only by very close application that its meaning can be obtained. It would probably be much more widely read if it were written in a simpler manner.

This volume will probably be of much greater value to the worker along purely scientific lines than it will to the chemist who is technically employed.

E. SUTERMEISTER

PROBLEMS IN PHYSICAL CHEMISTRY, with Practical Applications. By EDMUND B. R. PRIDEAUX, M.A., D.Sc., Assistant Lecturer in Education, University of Liverpool. New York: D. Van Nostrand Co. 1912. pp. xii + 311. Price, \$2.00.

This book was written at the suggestion of Prof. F. G. Donnan, and in order to gain some practical experience of the needs and capacities of students in familiarizing themselves with the fundamental laws of chemistry and in learning to think in a quantitative and accurate manner, the author conducted a "problem class" in connection with Prof. Donnan's lectures to senior students at Liverpool University. The book ranges practically over the whole field of physical chemistry, the titles of the various chapters being as follows: Units and Standards of Measurement, Thermochemistry, Systems of One Component, Mixtures, Gas Reactions, Reactions in Solution, Electromotive Force, and Kinetics of Molecular and Radioactive Changes. Each section is preceded by a brief introduction, containing a summary of such information as is necessary for an intelligent working of the problems. The choice of the latter has been restricted to such as can be solved by the aid of general principles and elementary mathematics. The data for most of the problems are taken from actual published investigations, references to which are given, and the student is also frequently referred to the original sources for discussions of the principles involved. Dr. Prideaux seems to have fulfilled his task admirably, and the book should prove of great assistance to the student of physical chemistry in teaching him to apply to actual problems the principles which he learns in the lecture room. The book is provided with a list of a few frequently used mathematical formulas and with a four-place table of logarithms and antilogarithms.

C. A. R.

EXERCISES IN CHEMICAL CALCULATION. By H. F. COWARD, D.Sc., Chief Lecturer in Chemistry, Municipal School of Technology, Manchester Lecturer in the Victoria University of Manchester, and W. H. PERKINS, M.Sc., Assistant Lecturer in Chemistry, University of Leeds. London: Edward Arnold; New York: Longmans, Green & Co. pp. v + 152.

This book does not differ materially from the various "chem-

ical arithmetics" found on the market except that some of the problems in the chapter on organic analysis involve the determination of structure from the empirical composition of a given substance and one or two of its derivatives. Some of these will tax the ingenuity of the student; indeed, it would be interesting to determine how many students could solve them without knowing the answer. Most of the problems are taken from examination papers for the various classes at Manchester, and it is probably in the preparation for such examinations that this book will find its greatest use.

C. A. R.

LES NOUVEAUTÉS CHIMIQUES POUR 1912. Nouveaux appareils de laboratoire, méthodes nouvelles de recherches appliquées à la science et à l'industrie. Par CAMILLE POULENC, DOCTEUR ÈS SCIENCES Avec 236 figures intercalées dans le texte. Paris: Librairie J.-B. Baillière et Fils. 1912. pp. viii + 338. Price, Fr. 4.

The present book is the 17th volume of this interesting annual. The same plan is followed as in preceding years. Almost any chemist looking through it is likely to discover some piece of apparatus described there which may prove very useful in his work.

C. A. R.

VAN'T HOFF PLAQUETTE

The Dutch sculptor, Pier Pander, has, at the suggestion of Prof. Cohen, made a splendid medal plaquette (bronze) of van't Hoff. Those desiring one will write a postal card to Herr Prof. Dr. Ernst Cohen, Utrecht, van't Hoff-Laboratorium der Rijks-Universiteit. The plaquette, which is reproduced from a marble portrait relief by the same artist, will then be sent, collect on delivery, by the firm supplying them. If 100 are sold, the price will be 6.50 marks apiece; if 200 are sold, the price will be reduced to 5.50 marks.

AVOGADRO PRIZE

The Royal Academy of Sciences of Turin, at the meeting of June 23, 1912, decided to offer the sum remaining from the subscription for the memorial to Amedeo Avogadro as a

prize for a work in chemistry bearing on the law of Avogadro which may be published during the triennium 1912-14 and to open a special competition for this purpose.

The conditions of the competition are the following:

A prize, entitled the Amedeo Avogadro Prize, of L. 1500 (\$300) (convertible, if desired, into a gold medal) is assigned to that competitor who shall have published in the triennium 1912-14 the best work in chemistry, either experimental or historical-critical, relating to the law of Avogadro.

The works presented will not be returned and must be written in one of the four following languages: Italian, French, German, English; and at least three *printed* copies must be sent before December 31, 1914.

The competition will end December 31, 1914, and the prize will be awarded during the year 1915.

None of the national resident or nonresident members of the Royal Academy of Turin may compete for the prize.

PAOLO BOSELLI
President